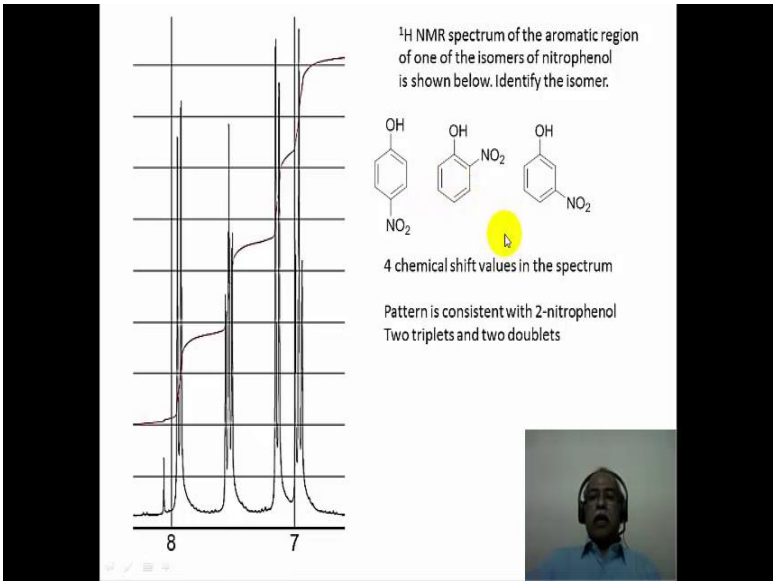
**Application of Spectroscopic Methods in Molecular Structure Determination**

**Prof. S. Sankararaman**
**Department of Chemistry**
**Indian Institute of Technology, Madras**

**Lecture - 15**
**Problem solving based on NMR**

Hello, welcome to module 15 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. This will be a tutorial session; we will try to solve some problems based on NMR spectroscopy.

(Refer Slide Time: 00:26)




Let us first go to the first problem. Here the NMR spectrum is shown; this is a proton NMR spectrum 300 megahertz proton NMR spectrum. The proton NMR spectrum of the aromatic region of one of the isomers of nitrophenol is shown below that is this particular spectrum here. This corresponds to one of the isomers of nitrophenol, we have to identify the nitrophenol isomer based on the spectral pattern that is given here.

Now, if we observe the spectrum very carefully in the region between 6.9 to about 8 ppm, there are 4 multiplets available and if you look at the integration it corresponds too,

for example, 1 hydrogen intensity this integration, this integration again corresponds to 1 hydrogen intensity, this also corresponds to 1 hydrogen intensity. Finally, the last one also corresponds to 1 hydrogen intensity, this is a nitrophenol molecule. So, it is a disubstituted aromatic compound, there are 4 aromatic hydrogen present. So, the integration essentially matches to the 4 aromatic hydrogen in the molecule. Now, what is important is that there are 4 chemical shift values associated with these 4 multiplets. So, whichever isomer we choose as the correct answer should have 4 different types of aromatic hydrogen in the system.

In other words, it has to be a, b, c, d kind of a spin system is what we are looking for in this particular problem. One can straight away rule out the possibility of the para nitrophenol because para nitrophenol has only 2 types of aromatic hydrogen, the 1 that is ortho to the hydroxy functional group and the ones that are ortho to the nitro functional group. So, this is a a a prime b b prime pattern. Please recall that a a prime b b prime pattern is symmetrical with respect to the center of the spectrum. This is not a symmetrical spectrum with respect to any centers of the spectrum. So, one can straight away rule out the possibility that this is the correct answer.

So, that leaves us with 2 other isomers namely the ortho nitrophenol and meta nitrophenol. Now in both the ortho nitrophenol as well as meta nitrophenol you have 4 different chemically non-equivalent hydrogen, hydrogen which is this 1 ortho to the hydroxy para and meta to the para to the nitro and meta to the hydroxy this particular hydrogen. Para to hydroxy and meta to nitro this particular hydrogen here. And finally, ortho to the nitro there is 1 more hydrogen. So, there are 4 spin system a, b, c, d kind of a spin system in ortho nitrophenol.

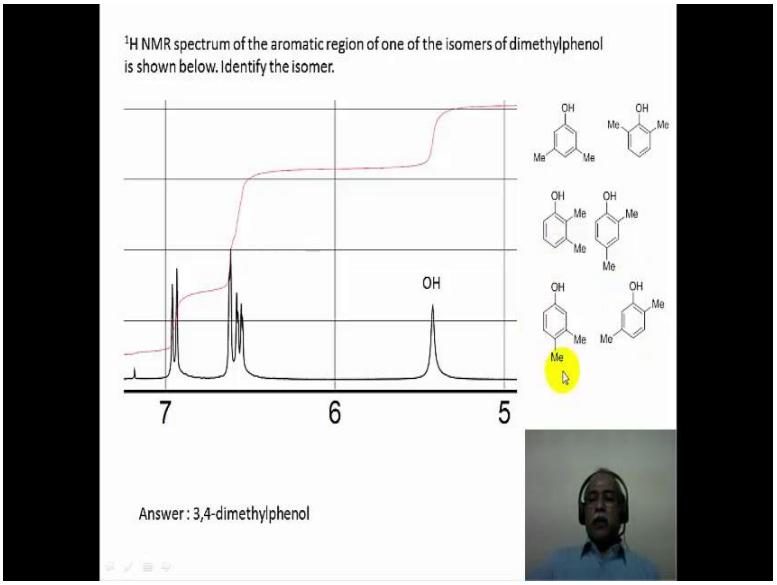
Similarly, in the case of meta nitrophenol also all these 4 hydrogen are chemically nonequivalent in nature. So, either of this spectra, either of this compound could satisfy the 4 chemical shift values that one sees in this particular spectrum. However, what one has to do to distinguish between these 2 isomers is to look at the pattern of the spectrum. If you look at the pattern of the spectrum there is a doublet kind of a multiplet in this region, there is a triplet multiplet in this region, there is another doublet multiplet in this region. Finally, another triplet. In other words, spectrum consists of 2 doublets with ortho

coupling which is the large coupling here. If one were to measure the coupling constant here, this would be roughly 7 to 8 hertz also. So, that corresponds to 2 doublets with ortho coupling and 2 triplets are also with ortho coupling.

Now, if you look at the spectrum, the 4 chemical shift values is satisfied by both these compounds, but the pattern is consistent only with the 2 nitrophenol of 2 triplets and 2 doublets. How do we know this? Because if you take this particular hydrogen this has an ortho partner, so it will be a double in nature and if you take the 1 which is ortho to the hydroxyl functional group that also will be a doublet because of the ortho coupling with the ortho hydrogen and if you look at the hydrogen in this position and this position. Let us say this hydrogen first para to the hydroxy and meta to the nitro this particular hydrogen has 2 ortho coupling partners. So, this will be essentially a triplet. Similarly, this hydrogen also has 2 ortho coupling partners. In most instances, the ortho couplings will be identical in nature, so this also would be a triplet. Essentially, you see these 2 triplets for these 2 types of hydrogens which are in the middle here and 2 doublets which are corresponding to the hydrogen ortho to the nitro and ortho to the hydroxy and ortho to the nitro functional group.

So, if you look at this compound the substitution pattern is meta. So, that leaves this particular hydrogen and there are no coupling partners ortho to this particular hydrogen. This would have appeared as a singlet or as a triplet with the very small meta coupling because of the 2 meta hydrogens present in the system. You do not see any kind of triplet with a very small meta coupling of the order of 1.5 to 2 hertz also. All this multiplets have ortho coupling that would correspond or that would be consistent only with the ortho nitrophenol has the correct answer.

(Refer Slide Time: 05:42)




Let us move on to the next question. Here again the aromatic region of a particular compound is shown here. This is a proton NMR spectrum of the aromatic region of one of the isomers of dimethylphenol. Which isomer is this question? Now, if you look at it carefully in the aromatic region between 6.5 to 7 ppm, there is a doublet with a large coupling which corresponds to the ortho kind of a coupling. This is corresponding to 1 hydrogen intensity and then there is a unresolved multiplet with a very small coupling with the 1 hydrogen intensity that is from this point to this particular point the inflection point that you have here that would correspond to 1 hydrogen intensity. Finally, there is a doublet which is sort of merging with the singlet which is again is different chemical shift value corresponding to 1 hydrogen intensity. Now this is a dimethylphenol, in other words it is a tri substituted aromatic compound. So, the remaining 3 protons is, what is seen in the NMR spectrum in the aromatic region of this particular region.

Now, if you consider these 2 isomers. Here, we have 3 chemical shift values, 1 chemical shift value close to 7 and 3 chemical shift values around 6.5 ppm also. If you look at these 2 structures, these 2 structures are symmetrical in nature. Therefore, this hydrogen which is ortho to the hydroxy and the other hydrogen which is ortho to hydroxyl, in other words that hydrogen in the 2 and 6 positions are identical chemically and the hydrogen in the fourth one is different from the other two. Similarly, the hydrogen in the 3-5 positions

are identical in terms of the chemical nature and the hydrogen in the 4th position is different. These 2 isomers will essentially gives only 2 chemical shift values because of the symmetry that is present in the molecule. There is a plane of symmetry as well as C2 axis of symmetry passing through the hydroxy functional group, this carbon and the para carbon in this particular molecule. Similarly, there is a plane of symmetry as well as C2 axis of symmetry passing through vertically along this line of this particular molecule. So, one rules out these 2 possibilities because it is not consistent with the substitution pattern that one sees.

So, that leaves us with 4 other isomeric forms of these particular dimethylphenol. If you look at the spectrum very carefully compared to benzene which comes to around 7.28 ppm or so. The chemical shift values of this phenyl are coming at lower delta value, this is essentially because this is an electron rich or electron donating substituent hydroxy functional group. The electron donating substituent essentially makes the 2 ortho positions in this molecule as an electron rich.

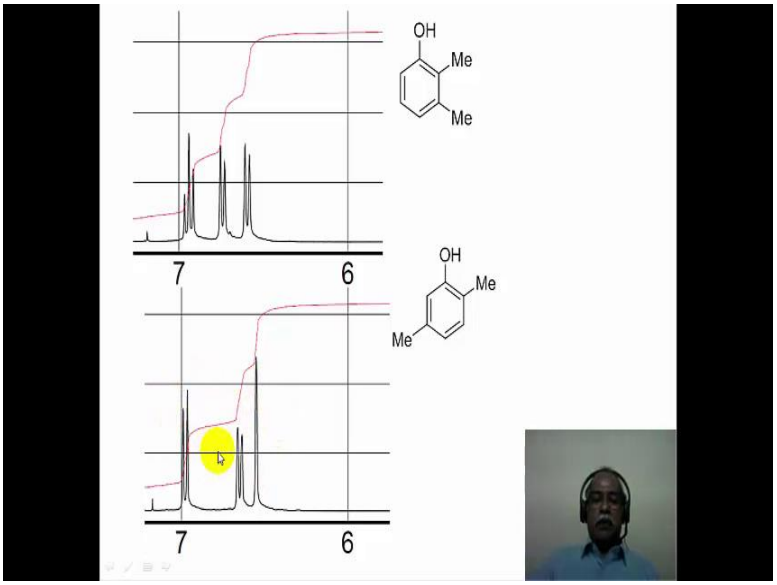
In other words, electrophilic substitution will occur only at this position that is an indication that they are electron rich in nature as a result of a higher electron density in the ortho position. These positions the hydrogens are going to be highly shielded. So, they come much lower in the value compared to the one that is in the meta position or in the para position. So, one can come to the conclusion because there are 2 hydrogens which are in the deshielded region of the aromatic region around 6.5 ppm or so. The phenolic compound that we deal with it should have at least 2 ortho hydrogens, ortho to the hydroxy functional group. If you take this phenol, there is only 1 ortho hydrogen. If you take this one, this also has only 1, this also has only 1.

So, that leaves us with this particular isomer with 2 ortho hydrogens to the hydroxy functional group. Perhaps, this would be the correct answer in terms of the choices among the 4 that we make based on that simple fact, that these 2 signals are essentially coming from a highly shielded carbon which could be the ortho carbon attached to the hydroxy functional group. Therefore, this is the only molecule where there are 2 ortho hydrogens to the hydroxy functional group, phenolic functional group. This would probably be consistent with the isomer that we talk about in this particular case. So, what

are the assignments if you take this particular hydrogen, this would be almost a singlet or it will have a very small meta coupling with this particular hydrogen. So, you see a singlet here with a very small coupling which is a unresolved coupling constant is what we do not see the coupling very clearly because it is fairly unresolved in nature. And if you take this hydrogen which is ortho to the hydroxy functional group that should have a large coupling with the meta hydrogen here, which is in this position here. So, that will be ortho coupling and that may have exhibit again is small amount of a meta coupling. So, this would be essentially a doublet and of a doublet. You see a doublet of a doublet with a large coupling constant which is the ortho coupling constant and small meta coupling is barely seen in terms of the resolution of the spectrum of this particular multiplicity that you see here, so this ortho hydrogen and this ortho hydrogen which are ortho to the hydroxy functional group or satisfying this spectral pattern.

Finally, you come to the meta hydrogen. Meta position should be relatively less electron dense compare to the ortho position because nitration does not proceed in the meta direction in the phenyl it proceeds only in the ortho positions not in the meta position. So the meta hydrogen comes at a higher side, slightly higher delta value and that has a large coupling constant with because there is an ortho hydrogen present in this. These 2 hydrogens couple together to form the doublet in this particular case, and this does not have any meta hydrogen it has only a para hydrogen. So, you do not see any further splitting up this doublet in this particular multiplet that you see here. Based on these facts, one comes to the conclusion that 3-4 dimethylphenol is the correct answer corresponding to this particular spectrum and of course, the OH peak is coming separately around 5.4 ppm or so. If you are curious about why we ruled out the other 2 isomers in this particular compound let me show you the spectrum.

(Refer Slide Time: 11:45)



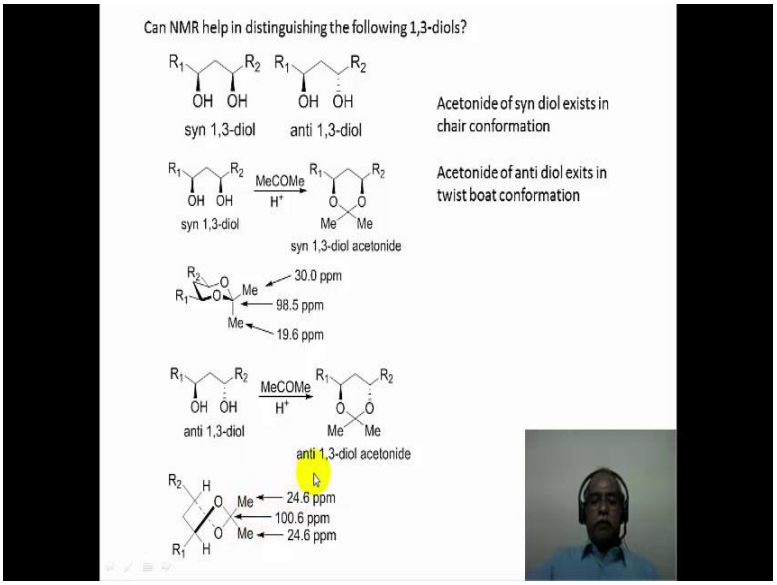

The pattern will be entirely different, if you take this isomer which is the 2-3 dimethyl phenyl as an isomer. This hydrogen which is flanked by 2 ortho hydrogen should either appear as a doublet of a doublet or a triplet. If it is an accidentally the 2 ortho J values are same. In fact, in this particular case, this triplet kind of looking a multiplet corresponds to this meta hydrogen which is coming at the highest delta value here. This hydrogen essentially is split by the 2 ortho hydrogens into a triplet that is seen here, and this hydrogen which is para. For example, will come at a higher delta value compare to the ortho hydrogen ortho to the hydroxy functional group. So, this is most shielded hydrogen which is coming as a doublet and this is the next shielded hydrogen which is para to the hydroxy functional group that also comes as a doublet.

Finally, this is coming as triplet and this is very characteristic pattern of 1, 2, 3 tri substituted derivative like this. Here you see only major ortho coupling in all the multiplets, there is hardly any meta coupling seen in this multiplets. Perhaps, if you go to higher resolution spectrum this is a 300 megahertz NMR spectrum. If we go to 500 or 600 megahertz spectrum maybe one could see the meta coupling which will be a very small coupling in this case.

Now, let us check the case of 2-5 dimethylphenol. The case of 2-5 dimethylphenol also, there is only 1 ortho hydrogen that is present here and that should essentially come as a singlet and that should be the lowest delta value. You can see a singlet with a lowest delta value around 6.5 or so in this spectrum. So please keep this spectrum in mind and compare it with this spectrum here, the singlet here is coming at a slightly higher delta value compared to this doublet that is because this has ortho coupling partner. This particular hydrogen which is the ortho hydrogen is coming at the higher delta value compared to this particular ortho hydrogen and because of this substitution that is present in the meta position. This is a relatively speaking less electron dense compared to this, one that is a reason this singlet it is coming at a higher delta value. Where as in this particular case, this artho hydrogen comes as a singlet at the lowest delta value then comes the para with an ortho coupling partner as a doublet.

Finally, the meta hydrogen also comes as a doublet around 7 ppm also in this specific. One can use the substitution pattern, if one can recognize this pattern properly then it is possible to distinguish between various isomers of aromatic compounds purely based on a simple first order analysis is what we have done, because most of this pattern look like a first order pattern. For example, a doublet look almost equal intensity this doublet also looks almost equal intensity. Although, there is a small roofing effect that is still seen in this spectra, one can afford to use a first order kind of a treatment to analyze this spectra. Let us move on to the next problem.

(Refer Slide Time: 14:43)




This is fairly complex problem, one need to understand certain chemistry aspects of the molecules to be able to answer this question. Can NMR help in distinguishing the following 1, 3-diols? This is syn 1, 3-diol and this is an anti 1, 3-diol, they are diol sterial isomers in terms of the sterio chemical relationship. The question is, can NMR distinguish these 2? One needs to know something about the chemistry of this molecule when it forms a ketol with acetonide, acetonide ketol when it reacts with acetone.

For example, if you take this molecule and treat it with acetone and a little bit of acid as a catalyst, the acid catalyst ketolisation will take place and the acetonide will be formed. The acetonide at the syn diol has a chair conformation because if you form an acetonide with acetone essentially you will form 6 membered rings. This is 1, 2, 3, 4, 5 and the acetone carbon will be the 6th carbon, so this will be a 6 member during. So, it exists in the chair conformation, where as in the case of the anti diol, the acetonide exists in a twist boat conformation. What do we mean by this chair conformation and twist boat conformation? This is a reaction I am talking about when the molecule is treated with acetone in the presence of trace of acid, it forms the cyclic ketol as the product which we call it as a Acetonide. The syn diol acetonide is shown here, the syn diol acetonide has this 2 carbon oxygen groups pointing in the same direction.

As a result of that it can exist in a chair form conveniently and if you measure the carbon 13 spectrum of this chair form, clearly one can see the equatorial methyl and the axial methyl separately. The equatorial methyl comes at a higher delta value compared to the axial methyl, this is something we have discussed with the earlier lecture series.

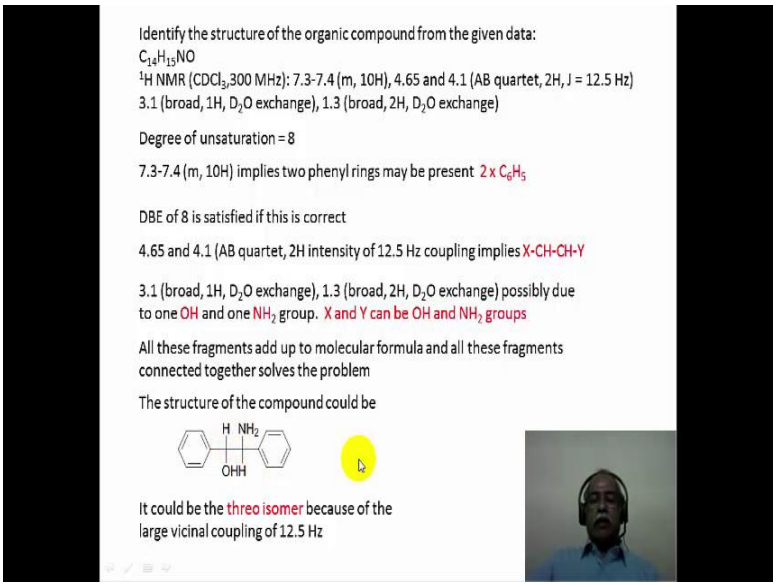
Finally, the acetal carbon comes around 98.5 ppm that is because it is connected to 2 oxygen it comes out a much higher delta value compared to this 2 methyl carbons which are terminal methyl carbons, one coming at 30 ppm another one coming at 19.6 ppm. So, the important aspect is the axial and the axial and the equatorial methyls are distinguishable in this particular compound, because of the chair conformation of this molecule. What happens with the anti diol? The anti diol also forms a cyclic acetonoide except this cannot exist conveniently in the chair conformation because this hydroxy C carbon oxygen bond and this carbon oxygen bond are anti with respect each other. So, you can see the anti relationship in the twist boat form of this particular molecule.

This is the most preferred conformation of this molecule and as a result of that if you look at these 2 methyl groups, they are coming at nearly identical chemical shift value because the distinguishing groups R 1, R 2 or further away from this center. As a result, these 2 methyls are nearly in the same chemical shift region after 24.6. So, if we can makes the acetonoide of these 2 alcohols, the 1 acetonoide that gives 2 different chemical shift value for this 2 methyls would be the syn alcohol because it exist in the chair conformation. The axial equatorial methyls are distinguishable, whereas the anti diol which when it forms the acetonoide forms essentially twisted boat kind of a conformation. Where in the 2 methyl groups are now almost equal and so they became chemical shift value. The acetonoide carbon of course, comes very close to 98. In other words it comes around 100 ppm, so the distinguishing factor is 2 methyl signals in this molecule and nearly only one methyl signal in this particular molecule because of the shape and the conformation of this particular derivative that has been made.

Here is an example, the alcohol itself is not directly identified as the syn or anti diol, the derivative session is done because the derivative has specific conformation that information is necessary to understand this molecule. So, once you know the conformation to be a chair or a twist boat and one can equally figure out the 2 different

chemical shifts for this conformation and only 1 chemical shift value for these 2 methyls in this particular conformation.

(Refer Slide Time: 19:07)




Now, let us try to solve a simple organic molecular structure using proton NMR spectroscopy alone. The molecular formula is given as C14H15NO from the molecular formula, one can arrive at the degree of unsaturation to be 8 in this particular molecule. Now the proton NMR spectrum shows 7.3 to 7.4 ppm multiplet of 10 hydrogen intensity most slightly this 10 hydrogen intensity of the multiplet, in the aromatic region would only imply 2 phenyl rings. So, let us assume there are 2 phenyl rings in this molecule. Now, this is a very characteristic chemical shift as well as the splitting pattern that one sees in the disubstituted derivative region around 4.65 and 4.1 the AB quartet is seen.

In other words, this corresponds to the delta value of A, this corresponds to the delta value of B. We have already seen the analysis of AB kind of a spectrum. So, this AB quartet has 2 hydrogen and it has a coupling constant of about 12.5 hertz or so. This would only be corresponding to a system like this one, this is AB system and the 12.5 hydrogen is because of the conformational aspect of this molecule.

We will come to that the little later. So, one comes to the conclusion that this is a disubstituted derivative of this kind. There is one more substituent to satisfy, if valence 4 of this particular carbon that is shown here and this 2 phenyl groups are probably the substituents which are the additional substituents the disubstituted compound. This particular pattern recognition of AB quartet with 2 hydrogen intensity in this chemical shift region has to be only this kind of a substitution pattern, one should recognized it, in other should be able to solve this particular problem.

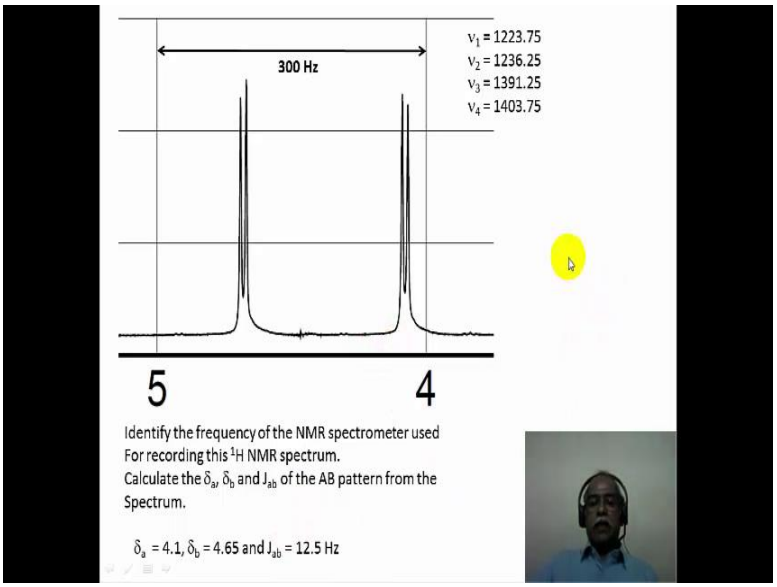
Now, we need to identify these 2 groups x and y that is fairly easy to do because there are 2 very distinguishing feature in this particular spectroscopic data 3.1 broad. 1 hydrogen intensity of D2 exchange because oxygen is present in the molecule, most likely this is OH functional group. 1.3 broad 2 hydrogen intensity of D2O exchange there is nitrogen present in the molecule. So, most slightly the 2 hydrogen intensity exchangeable hydrogen is only probably due to NH2. So, the x and y can be OH and NH2 respectively in this particular fragment that we see here. If you put in all these fragments together that is OH, the NH2 the C2H2 and the C6H5 that essentially satisfies the molecular formula which is C14H15NO, it also satisfies the degree of size and unsaturation because 2 phenyl groups. Each phenyl group corresponds to 4 degree of unsaturation of the 2 phenyl group will take care of the degree of unsaturation in this molecule. There is no other unsaturation in terms of carbonyl functional group and so on.

In this molecule because the degree of unsaturation is already satisfied by that 2 phenyl groups in the system. So most likely structure is this particular structure, the additional 3 groups that needs to be attached to this CH carbons here or the phenyl groups and the x and y are OH and NH2, so this is essentially the molecule. The reason one sees a very large coupling for this vicinal coupling is because if the vicinal coupling is anti with respect each other. In other words, in the conformation if these 2 hydrogens are anti, in other words anti conformation is what I am talking about. This is 1 hydro 180 degree dihedral angles what we are referring to, such a high dihedral angle could probably be responsible for this 12.5 hertz in this spectra.

We have already seen how to distinguish the erythro isomer from the threo isomer in the earlier sessions of the NMR spectroscopy. This is based on the 12.5 heads hydrogen

coupling vicinal coupling, one can come to the conclusion thus it could be a threo isomer because the large vicinal coupling constant because only in the threo isomer you have a conformation where the 2 hydrogens are trans or anti with respect to each other and that would correspond to this 12.5 hertz. So please go back to the earlier lectures where we talked about stereo chemistry determination using NMR spectroscopy and refresh your memory to identify this 12.5 hertz coupling corresponding to the anti conformation of this particular molecule.

(Refer Slide Time: 23:46)




Now, this is a fairly simple problem. A spectrum is given here and from the look of the spectrum we can see here, there is a doublet here and another doublet here and this doublet and this doublet essentially forms AB quartet kind of a spectrum because with respect to the center this is symmetrical and the other side, you see a slide roof effect in this project. So, this as a slide second order affect, the four frequency is given mu1, mu2, mu3 and mu4 corresponds to the frequency of this four lines starting from here. This is the 1223.75 hertz corresponds to the first peak the second peak is mu2, this is mu3 and mu4. So, the identification of the frequency of the 4 lines that are seen in the spectrum is very clearly given in the problem itself.

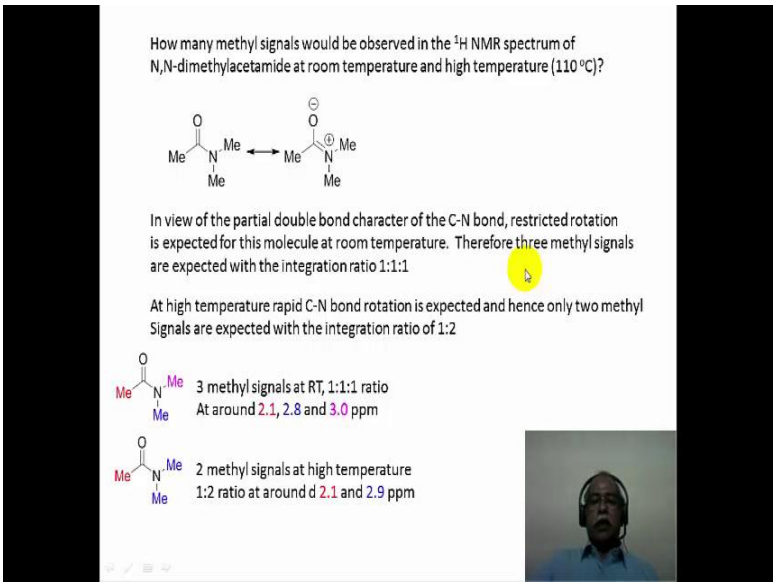
The question is to identify the frequency of the NMR spectrometer used for recording this particular spectrum. So, how do we do that? This gap which is 1 ppm that is from 4 ppm to 5 ppm corresponding to the 1 ppm gap corresponds to 300 hertz in terms of the spectral width of 1 ppm. So, if the spectral width of 1 ppm corresponds to 300 hertz, what would be the spectrometer frequency? Please recall the definition of chemical shift; chemical shift expressed in delta ppm corresponds to the change in the chemical shift expressed in hertz divided by the spectrometer frequency. The spectrometer frequency is what is asked in this particular problem. So, 300 divided by 1 ppm would correspond to essentially 300 megahertz. This spectrometer essentially is 300 megahertz NMR spectrometer. So, this is a question that one should be able to easily answer based on the fact that the 1 ppm gap of 300 hertz would correspond to 300 megahertz NMR spectrometer.

The other question is to calculate the delta A, delta B and J ab from the NMR spectral pattern. One has to use the equation that we had described earlier that is the difference between the chemical shift value of delta A and delta B. In other words delta of AB would correspond to square root of mu4 minus mu1 multiplied by mu3 minus mu2. So, that will give you the separation between A and B. So, if you take half the separation and add it to the center of the center frequency, center frequency can be easily obtained by the average of the mu2 and mu3. So, let us call this as C, which is the center C plus half of the delta, delta AB would correspond to 1 frequency that is the delta A and C minus half of the delta, delta by divided by 2 would corresponds to the other frequency which would be delta B. So, one this is something we have already solved during the course of the NMR spectroscopy lecture.

So please refer back to the arithmetic that needs to be done using the 4 frequency values in order to be able to extract the delta A, delta B and the J ab. What is J ab in the spectrum? You take the difference between line one and line two, that is J ab which should be identical to line 3 and line 4 difference which is also J ab. I have done this calculation, the delta A should come out to be 4.1 and the delta B should come out to be 4.65 which is this particular delta and this is 4.1 and 4.65 and the J ab corresponds to 12.5 hertz, which is a simple arithmetic of subtracting these two frequencies or these 2 frequencies would give you essentially 12.5 hertz as the coupling constant value. So, try

to work out this problem yourself and satisfy yourself and that this answer given is a correct answer for the arithmetic that needs to be done in order to extract the information of delta A and delta B as well as the J ab from the spectral data that is given.

(Refer Slide Time: 27:35)




This is fairly simple question. Most of you should be able to answer this without even thinking about it. How many methyl signals would be observed in the proton NMR spectrum of NN dimethylacetamide at room temperature and at high temperature? In other words, at room temperature how many methyl signal and at high temperature, 110 degrees how many methyl signal? What is NN dimethylformamide? This molecule is NN dimethylacetamide, remember the nitrogen lone pair participates in the delocalization on to the oxygen and that gives a resonance structure which is this resonance structure. So, the molecule has a partial double bond character between carbon and nitrogen and because of this partial double bond character there will be restricted rotation that can be expected in this molecule at room temperature. In other words, the carbon nitrogen bond will not freely rotate, if the carbon nitrogen bond does not freely rotate then one can expect 3 different signals for the methyl. One corresponding to this methyl, one corresponding to this methyl which is trans to the oxygen.

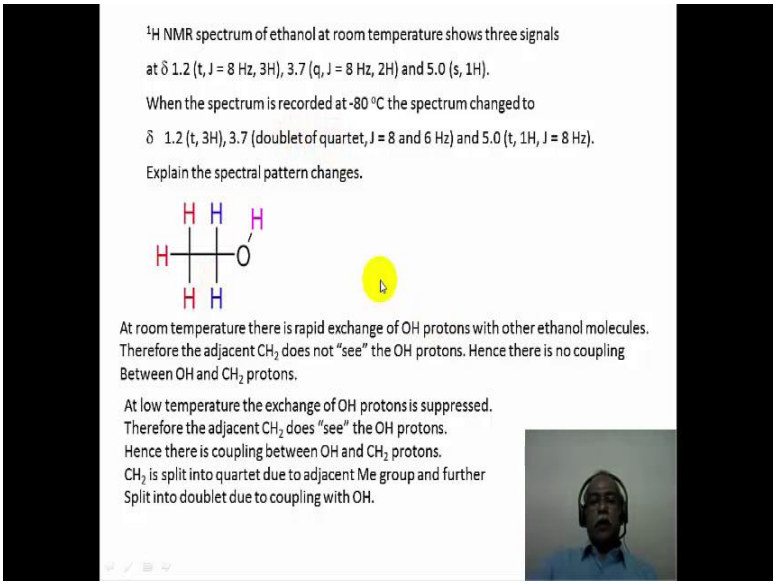
The other one corresponds to this methyl, which is cis to the oxygen. So, at very slow rotation these 3 methyls should be distinguishable. Anyway, these 2 methyls are distinguishable from this methyl there is no concern about that. Between these 2 methyls, 1 is cis the other one is trans to the oxygen. So, they should also be able to distinguishable in the NMR spectrum. So, one would expect 3 line patterns for the three methyl, the ratio of 1 is to 1 is to 1.

Now, what happens when you increase the temperature the rapid rotation of the carbon nitrogen bond takes place that exchanges these 2 methyls in terms of their relative position and the NMR is no longer able to distinguish these 2 methyl groups from one from the other and as a result of that at high temperature because of the rapid rotation of the carbon nitrogen bond only two methyl signals are expected in the ratio integration of 1 is to 2. One corresponding to this two corresponding to this methyls. So, this is a room temperature spectrum 1 is to 1 is to 1 ratio.

In fact, the methyl which is the acetyl methyl comes at 2.1 ppm, the chemical shift value and structure methyls are color coded, one can match the colors with the corresponding methyl. The blue methyl which is the trans to the oxygen comes at a lower delta value compared to the one which is cis to the oxygen which comes at a higher delta value at high temperatures because of the rapid rotation these 2 methyls exchange they become indistinguishable. So, they come at the value of 2.1 for the red methyl and the blue methyl comes around 2.9. You can see here the average of 2.8 and 3 corresponds to about 2.9. So, when the coalescence takes place and you get a sharp singlet for the 2 methyl, you get the average value of the individual methyl which seen separately at room temperature.

So, this is a fairly simple problem, something by NN dimethylformamide we have discussed. This is an example of NN dimethylacetamide which also has restricted rotation around the carbon nitrogen bond.

(Refer Slide Time: 30:42)




Moving on to the next problem, here we have an NMR spectrum of ethyl alcohol is being discussed. At room temperature, the ethyl alcohol spectrum is shown here. This is the normal ethyl alcohol spectrum that one would expect. In other words, the CH3 will be a triplet, the CH2 will be a quartet with a coupling constant which is vicinal coupling and the CH. So, OH will be a broad singlet usually is exchangeable hydrogen. So, the 1.2 corresponds to these 3 red hydrogen, the 3.7 corresponds to this 2 blue hydrogen, the magenta hydrogen corresponds to 5.0 ppm delta value, it is a singlet of 1 hydrogen. In other words, there is no coupling between the magenta hydrogen and the 2 methyl hydrogen. When the spectrum is recorded at minus 80 degree the spectral pattern changes, explain these spectral pattern changes in your answer. This is the question that explains the patterns that you observe here.

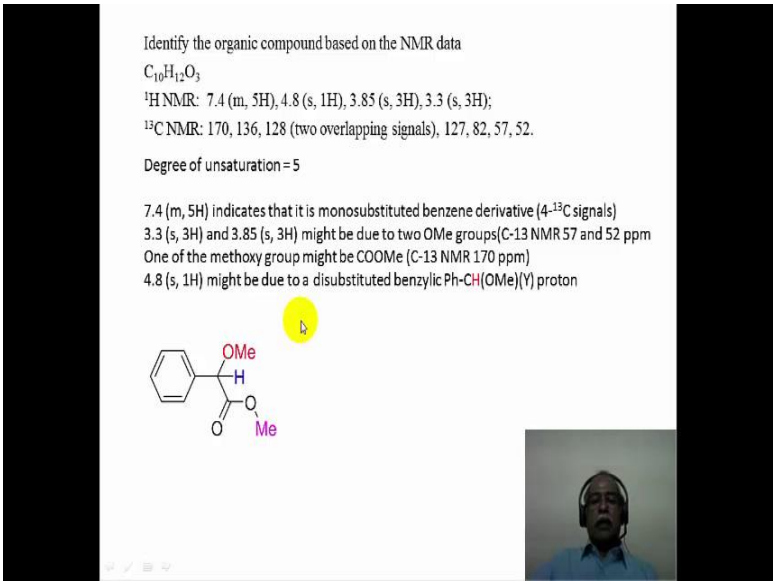
The pattern is easy to explain that methyl group comes as a triplet because 2 adjacent hydrogen and the methylene group comes as a quartet because of 3 adjacent hydrogen. This hydrogen does not couple because it rapidly exchanges and undergoes the positional character of this hydrogen is questionable under the conditions of rapid exchange. So, one does not see the coupling between the 2 methyls and the 2 methylene hydrogen and the magenta hydrogen here. However, when you cool it to minus 80 degree the exchange process is considerably slowed down, in other words the magenta hydrogen spends more

time on this particular oxygen rather than hopping from 1 oxygen to another oxygen of another molecule and so on. Since the resonance time is much larger at low temperature for the magenta hydrogen to stay on the oxygen, these 2 methylene groups essentially see the presence of this particular hydrogen. Hence, they undergo splitting by the magenta hydrogen also.

So, what is the multiplet that is seen? The 1.2 is still a triplet because of adjacent 2 hydrogen see what happens to the 3.7 signal that becomes a doublet of a quartet. Why is that a doublet of a quartet? It is a doublet because of the magenta hydrogen with the coupling constant value of about 8 hertz and it is a quartet because of the 3 hydrogen that is coupled, the coupling constants are different. This coupling constant OH and the CH2 coupling constant is different from CH2CH3 coupling constant, one is 8 hertz the other one is 6 hertz. So, 1 C is a doublet of a quartet for the methylene when the spectrum is frozen at minus 80 degree.

In other words, the exchange process is frozen are slowed down considerably at minus 80 degree. Even more interesting is this OH hydrogen which is coupled to now to the methylene is mutually coupled. So, the OH hydrogen also appears as a triplet of 8 hertz intensity, in this 8 hertz coupling constant in this particular system. So, at room temperature there is a rapid exchange of OH proton with other ethyl alcohol molecule therefore, the adjacent CH2 does not see the presence of the OH and hence there is no coupling between the OH and the CH2. At low temperature, the exchange of which process proton is suppressed therefore, the adjacent CH2 does see the presence of the of OH proton. Hence, there is coupling between OH and CH2, CH2 is split into a quartet due to adjacent methyl and further splitting to a doublet because of the adjacent OH. So, the OH coupling and the CH3 coupling is what makes this multiplet as a doublet of a quartet in the low temperature NMR spectrum of this particular molecule.

(Refer Slide Time: 34:22)




Now, let us look at one more problem. Here we have to identify the organic compound based on the NMR data that is given here is a fairly simple problem. If you logically approach this problem, it will turn out to be a simple problem. If you try to somehow solve it then you may be end having up with troubles.

Now, the degree of unsaturation is clearly 5 in this molecule. You can calculate from the molecular formula at the degree of unsaturation, the 7.4 multiplet 5 hydrogen is a very characteristic monosubstituted benzene derivative. It also matches with 4 NMR signal for the monosubstituted phenyl derivative, two overlapping signals at 128, 136 and 127. These 4 signals essentially correspond to a mono substituted benzene derivative in terms of the carbon signal. The 170 corresponds to a carbonyl functional group most likely an ester kind of acid derivative is what we are referring to here. So, 4 unsaturation corresponds to the phenyl ring and the 5th unsaturation probably corresponds to ester carbonyl functional group which is consistent with 170 ppm signal in the carbon 13 spectrum.

Now, let us see the 3.85 and 3.3 are characteristic regions of the methoxy functional group, since there are 3 oxygen present here, we can account for 2 methoxy because the chemical shift value 3 and above 3 to 4 is very typical of OC, is any kind of a region. So,

3.3 and 3.85 might be due to 2 methoxy functional group and that collaborates with the carbon 13 spectrum also where you have 57 and 52 corresponding to the 2 methoxy functional group in the carbon 13 and 1 methoxy might be because of an ester functional because you have 170 ppm signal present in the carbon 13 spectrum and if you look at this methoxy this as a higher delta value compare to this methoxy. So, this is probably an ether methoxy OMe3, whereas this is COOMe is the kind of a spectrum that you have. So, 4.8 might be due to a disubstituted benzylic derivative. This is a highest delta value 4.8 among the aliphatic signals that you see here. So, that is why I am saying that this is a disubstituted, one of the substitute is methoxy the other substitution might be COOMe, the third substitution is phenyl. So, essentially you have benzylic hydrogen with two substitutents which push the chemical shift value all the way up to 4.8 ppm.

So, putting all these fragments together you have two methoxy functional group 1 methoxy here and 1 methoxy here, 1 phenyl substituent here and this is CH which is coming as a singlet around 4.8 ppm of 1 hydrogen because this is triply substituted benzylic position is highest delta value that one sees in this particular spectra and the double bond unsaturation is also satisfied 4 for this ring and 1 for the carbonyl functional group. If you look at the carbon 13 there is one signal at 82 that signal is because of this particular carbon which is a tertiary carbon here that corresponds to the carbon attached to oxygen attached to a carbonyl functional group and it is also benzylic. So, all these 3 substitute and essentially push the chemical shift value of this carbon more than 50 or 60 it comes around 82 in this particular case and thus we solve the problem corresponding to this particular data that is given.

It can always go back and see whether the structure satisfies the data that you have in this molecule or if you have any other suggestions based on this spectral data which comes out to be a different structure. Let me know, if it is logically correct then we will take care of it. So, what we have seen in this particular module is a tutorial session of solving certain very simple organic compounds. Some simple dynamic processes associated with organic compounds using NMR spectroscopy.

Thank you very much for your kind attention.