Interpretative Spectroscopy

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Lecture 55

Problems and Solutions-5

Hello everyone, welcome you all once again to MSB lecture series on Interpretative Spectroscopy. So, I have been looking into problems and finding right solutions with combination of data taken from more than one spectroscopic methods. So, let me continue solving more problems in this lecture as well.

I have a problem here

29. Following four compounds are put in four unlabeled vials and some information is given about their ^{1}H and ^{13}C NMR spectra. So, now we have to identify by looking into the information that is provided for right or appropriate molecules. So, here four molecules are there, they are all chloro derivatives of propane: **1,1,dichloropropane, 1,2,dichloropropane, 2,2,dichloropropane and 1,3,dichloropropane**.

It seems with the 2 chlorine and propane we have looked into all four possible isomers. First what we should do is draw the structures of all and identify how many different type of signals are there in ^{1}H NMR as well as ^{13}C NMR spectra in each case.

First let us focus our attention on ^{1}H NMR of first molecule here: This is 1,1-dichloropropane. If you see here, all the three hydrogen atoms are different, as a result in ^{1}H NMR, we expect three signals and also in ^{13}C also we anticipate three signals here. Then if you look into it, most deshielded is this one. This one should give a **triplet** coupling with this one. So, that information let us write down here. **So, the lowest field signal is a triplet here.** This information let it be there. Now we shall move on to the second one 1,2-dichloropropane again here three signals are there in case of both ^{1}H as well as ^{13}C.

And if you look into this one here: this is the lowest field signal this one is coupled equally with these two as a result it would show six lines.

Now let us look into this molecule here of course, you can see C_2 axis of rotation, as a result only half we should consider. So, these two are identical only one signal will be there and then two carbon signals will be there here only one signal this is unique compared to the rest of them. Now let us look into it again we have C_2 axis of rotation and then here we have two type of signals for methylene with chlorines on both side and this methylene. And then of course, if you look into the NMR of signal of this one this would show a quintet and then these two will show a triplet this should be like this and then two signals will be there.

This one is a lowest one is also a triplet. We have to identify and tick the corresponding chloro derivative from these four columns. For your information I have provided simulated ^{1}H NMR as well as ^{13}C NMR for each compound. You can see here a triplet is there and for this one quintet is there. We have a triplet here this is for 1,1-dichloropropane here. So, this one would show with both are coupled equally 4. So, 5 lines it is showing and then this is showing a triplet and this also showing a triplet here and then we have 1 2 3 signals are there.

And then we look into here this one of course, this one is the lowest one this will couple with both of them as a result it shows a 6 lines and then this geminal coupling is there as a result you can see here it is going like this. So, there is first second order splitting is there and then we are seeing for this one a doublet here and then of course, here 3 are there 1 2 3 and here also 1 2 3 signals are there. So, now 3 signals between 0 to 5 lowest field signal is a triplet. So, that information given is for this molecule here and similarly here this gives a 6 lines. So, information provided is this one and in case of this here this shows a singlet ^{1}H NMR and then we see 2 ^{13}Csignals and in this case this one show a quintet here and then these two would show triplet here.

And then for this one the lowest one is a triplet and then 2 signals are there that means, here one singlet at 1.2 this is 2,2-dichloropropane and here it is 1,3-dichloropropane. So, now we shall come back to this the answer for the first one is 1,2-dichloropropane answer for the second one is 2,2-dichloropropane answer for the third one is 1,3 di-chloropropane and then for the last one answer is 1,1-dichloropropane. So, this is how we can use this information draw the structure look into the symmetry and identify how many different distinct groups are there and then arrive at the answer it is very simple, right.

32. Now, let us look into another example here. With respect to the ^{1}H NMR spectrum of $C_{10}H_{12}O_2$ (at 90 MHz), answer the following questions.

1. How many discrete groups of proton signals are there except the reference?
2. What is the multiplicity of the highest field signal?
3. The sample has a singlet at 3.8 ppm. It is value in Hz is
4. What structural feature is suggested by the singlet at 3.8 ppm.

   a. **CH_3—C=O** **b. -CH_2-** **c. -O—H** **d. -O—CH_3** **e. C—CH_3** **f. C=C—H**

5. Predict which of the other signals is coupled to the quartet at 2.9 ppm?

   1.2 3.8 6.9 7.9 ppm

6. Predict the number of protons present in each signal

   7.9 6.9 3.8 2.9 1.2ppm

So, now just look into carefully here we have 1 2 3 4 5 signals are there here apart from TMS, TMS is a reference that is at 0 we have 5 signals are there.

So, now how many discrete groups of proton signals are there except references answer is 5 here.

So, then what is the multiplicity of the highest field signal highest field signal is here: This one highest field signal more shielded one close to TMS that is triplet.

The sample has a singlet at 3.8 ppm, its value in Hz is

To convert ppm into Hz, what we have to do is, we have to multiply that by field strength 90. 3.8 into 90 (3.8 x 90) would give you the Hz that is 342 Hz.

What structural feature is suggested by the singlet at 3.8. So, 3.8 if you look into it.

So, this one is not coupled with anything and we have oxygen probably the options are given here we have to identify which one. So, now since it is not coupled with any other proton that

means there is some electronegative atom comes in between two carbon atoms and here obviously we have other hetero atom is oxygen. So, it has to be OCH_3 next predict

Which of the other signals is coupled to the quartet at 2.9 ppm. So, let us look into quartet at 2.9 ppm. So, we have a quartet and if quartet is there in the neighborhood, there should be 3 protons. So, for example, if you consider CH_2CH_3 and if you are looking into this one this would be a quartet and this will be a triplet. Then we have to find out which is coupled with this one here; coupling constant values are not given. By simply looking into the signals and the separation of the individual lines in this multiplet we should be able to tell, which is coupled with this one and that is 1.2.

Next predict the number of protons present in each signal 7.9, 7.9, 2 are there. So, that means number of protons here is 1 and here also 1 and then in case of 6.9. Then 3.8, by integration we should be able to 3 and then 2.9, 2 and then 1.2 is 3.

Now with this information we have to identified what molecule it is what we can do is hydrogen index deficiency we can look into it. So, that would say 11 minus 6 = 5 (11 -6 = 5). So, 5 indicates one ring is there plus 4 double bonds are there. So, this information is there with this information and by looking into these 5 different type of signals, then one ring is there it has to be aromatic group something like this and then we have two identical ones in the aromatic region. If two identical ones are there, that means probably this one, this one , we should consider these two are one type and these two are another type. So, it goes around 4 protons and then CH_3 CH_2 CH_3 is there.

That means this one here 3 and then here this one is there that indicates there may be something like, 12 are there H12 and then O2 and then we have C10. So, that means here 1 2 3 4 double bonds are there and then one ring is there. This also satisfies rule whatever we are talking about. Hydrogen deficiency 4 is satisfied and then these are identical now and these two are coupled with this to show two doublets this one doublet and this one doublet they are very minute differences in the chemical shift. They are coming together and then this is showing a singlet here and then this is showing a quartet and then this is showing a triplet here.

So, this is the molecule. So, this is how we can identify the molecule and then we can also answer simply by looking into even before identification of the molecule we should be able to answer the questions that are listed here.

33. Now let us look into another problem related to phosphine complex of rhodium with coordination number 5 and rhodium is in +1 state because 4 trimethyl phosphines are there, neutral ligands, and then we have one methyl is there. So, rhodium is in +1 state. So, for this one very interesting two spectra are recorded. One at room temperature and another one at -80 ^{o}C. At room temperature a doublet is observed and at -80 ^{o}C a doublet of doublets and quartet of doublets. That means two signals are observed.

Now we have to see what are the right geometries that explains these two kind of situations in case of ^{31}P NMR.

Well when we have coordination number 5, only two options are there one is it can be square pyramidal and other one is trigonal bipyramidal. Since it shows a doublet and also we should remember the fact that ^{103}Rh with I equal to half (I = ½) is 100 percent abundant and usually rhodium to phosphorus coupling comes in the range of 150 to even 300 hertz. That means with much larger coupling, this doublet indicates probably all four trimethyl phosphines are equally coupled to rhodium resulting in a doublet. That means we have to write a right kind of structure in which all four trimethyl phosphines are identical.

We just look into it this, a square pyramidal in which all 4 phosphines are in the plane and they are identical. Here they couple with this one to show a doublet here.

Now let us look into another example. Now doublet of doublet means probably it is not retaining at -80 ^{o}C, it is going to geometrical isomerism and other alternative is trigonal bipyramidal. When we go for trigonal bipyramidal we have several options. Let us write one or two options to begin with.

So, this is trigonal bipyramidal, I have drawn one isomeric form where all 3 trimethyl phosphines are in plane and one in axial position. So, now let us look into this one here, these 3 are identical and they first couple with rhodium to give a doublet and are equally coupled with axial one another doublet comes here. So, this is $^{1}J_{RhP}$ rhodium-phosphorous coupling and then this spacing is $^{2}J_{PP}$ coupling here. So, we get a doublet of doublet yes, this is the right structure I have drawn. Next this is for equatorial put E, let us look into axial one now.

So, now this would first couple with rhodium and then it is coupled with three PMe_3. Use 2n*I* plus 1 (2nI + 1) rule; 4 lines should be there. So, that means basically. So, this spacing is $^2J_{PP}$ coupling, so doublet of quartets. So, this is how you can explain and draw a spectrum and then understand the problem. Here at -80 ^oC, it shows 2 signals having trigonal bipyramidal geometry one is doublet of doublets and other one is doublet of quartets. So, at room temperature, it isomerizes to square pyramidal geometry having all 4 trimethyl phosphines in the plane and shows just coupling with rhodium.

34. Let us look into another example. ^{195}Pt NMR is shown in the Fig.1 for the platinum complex. Assign the coupling constants.

This I think I already discussed this while looking into NMR problems. Let me recall again and tell you about 195-platinum NMR and how to interpret. So, spectrum is already given here 195 platinum (^{195}Pt) NMR spectrum and the structure is also given only you have to interpret and explain why they are giving two triplets of equal intensity.

Here if you just look into it, nitrogen atoms, one is ^{15}N, which is already designated. For this one I equal to half (I = ½). This is coupling first let us say with ^{15}N. Now we have to see this is split into triplets. It (platinum) does not have anything in the close vicinity. We have carbon, carbon cannot show ^{13}C, is only 1 percent.

With this that information, the next target is two bonds away from platinum, that is N. If it is not labeled anything we can assume this is ^{14}N and ^{14}N has I equal to 1 (I = 1). If it couples, it should show three lines of equal intensity as per 2nI+1 rule. That means platinum is coupled both with ^{15}N as well as ^{14}N. ^{15}N first splits it into a doublet and each line will be further split into triplet of equal intensity by ^{15}N. So, this how you can interpret and understand the coupling constants and eventually the data that is provided.

35. Interpret the spectrum below for the compound $[(CH_3Pt(CH_2{=}CH_2)\{PPhMe_2\}_2]$. Justify all splittings. Is this the cis or trans isomer? (^{31}P, 100% abundance, I = 1/2; ^{195}Pt, 34% abundance, I = 1/2).

Now, let us look into another example here. Interpret the spectrum for the compound that is shown here, is a platinum compound again four coordinated one, justify all splitting. When 4 coordination is there, we have to see whether it is cis or trans. Let us write first trans. Here we just look into this compound here this is a square planar complex. if I do C_2 axis of rotation

both the phosphorus in the trans isomer are magnetically and chemically equivalent. And if you look into phosphorus NMR they will just show a singlet that is singlet and then platinum satellites will be there.

That means it is has to do nothing with ^{31}P NMR spectrum. Of course, 195-platinum (^{195}Pt) abundance is 34 percent, that is NMR active with I equal to half and rest 196 is 66 percent and is NMR inactive.

Three signals are there. If you look into the chemical shift range it appears like probably a ^{1}H NMR spectrum. If it is ^{1}H NMR spectrum, how it should look like. First, we should look into methyl group and if the 3 hydrogen atoms are coupled with these two P to give a triplet here. So, they give a triplet and then it would couple with platinum. When it couples with 195-platinum it will be split into a doublet.

That means basically you will see something like this here. This pattern is more or less same for all of them. So, one is for this methyl triplet this is for I equal to 0 (^{196}Pt) and this is for I equals half (^{195}Pt). This is Pt-H coupling. So, now this pattern is same for all, but we have to look into number of hydrogen atoms. This is 3. So, this is one here and then here 6+6 =12 then here we have 4.

That means all of them are behaving in a similar way and all of them are coupled with ^{195}platinum; 34 percent showing singlet and then probably that is split into triplet and then this one also singlet that split into a triplet here. So, this is how you should be able to explain the NMR. The NMR given is of ^{1}H that represents CH_3, ethylene and methyl. Then the ratio will be 3:4:12.

So, let me stop now and come back with more examples in my next lecture until then have a great day.