Interpretative Spectroscopy

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Lecture 54

Problems and Solutions-4

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. This is 54th lecture. In the last couple of lectures, I started solving lot of problems and giving different kind of solutions to understand interpretation. So, let me continue from where I had stopped. Let me take some more interesting problems associated with IR, Mass Spectrometry as well as NMR.

23. Now, I have a question fully based on IR data. Determine the structure or possible structures for a compound with formula $C_5H_{10}N_2$ and the spectra spectrum is given here. As I had mentioned, first you should look into the molecular formula, and find out hydrogen deficiency index.

So, that formula, I am sure you are familiar. If you just consider here 6, this will be 5, here nothing is there plus 1 here. So, now 2 is the deficiency that means possibly there can be a ring or two double bonds or there can be triple bond.

So, let us look into it now.

First let us try to analyze there is a signal in the region 2300 region, that means N is there, you can think something like C triple bond N (C≡N) nitrile group. This will also tell you about the presence of CH and then we have several peaks in the fingerprint region. It is very difficult to identify without much knowledge and also we can see nothing is there around 1600. That means possibly there is no aromatic group here, if the aromatic group is not there, then possibly **Hydrogen Index** two means there should be a triple bond which is there. So, now you read out some of the points I have made about this problem when only minimum data is given.

The index of hydrogen deficiency is calculated to be 2

A glance at the spectrum shows a prominent peak near 2250 cm^{-1}. The only functional group appearing near this value is a nitrile (C=N) or an alkyne (C=C).

An alkyne would appear closer to 2150 cm^{-1} while a nitrile would appear at the value observed in the spectrum.

Since the index of hydrogen deficiency has a value of 2, that fits a compound with a triple bond.
The remaining nitrogen atom would likely be an amine.

Unfortunately, the region between 3600 and 3200 cm^{-1} does not reveal easily what type of amine may be present.

The region is often obscured by the presence of water in the sample, or from weak overtone peaks from other parts of the molecule.

However, a primary amine (RNH_2) should show a prominent doublet while the secondary amine (R_2NH) should show a singlet.

Since no prominent peaks appear between 3600 and 3200 cm^{-1}, we can conclude that this compound is a nitrile (C=N) with an attached tertiary amino group (R_3N).

So, possibly it is not primary amine or secondary amine it should be a tertiary amine. In that case the structure is going to be something like this.

So, dimethyl amino group is there and then we have a C≡N. For curiosity, I have also taken ^1H NMR for this one and ^1H NMR you can identify, 1 2 3; three different type of signals are there. If we just look into these two, these two should show a singlet that comes here, and then this would show a triplet and this would show a triplet.

So, both are CH_2. So, both of them will show a triplet, two triplets are there. That is it. The problem is solved now this is the structure and this nicely fits into this ^1H NMR spectrum shown here. For curiosity I also took ^{13}C NMR spectrum for this molecule here and look into it and identify how many nonequivalent signals are there?

We have 1 2 3 4 and 4 can be assigned very nicely and this is 119. This comes here and then these two will be here because they are on N and then this is close to N. So, it comes here and then this is coming here. Expected spectrum in case of ^{1H} as well as ^{13}C. So, this is **3-(dimethylamino)propanenitrile**.

24. For each of the compounds, indicate the number of actually distinct groups of carbon and hydrogen atoms.

It is not to specifically tell the chemical shift values. It is very difficult, nobody will ask you all the information. Only thing is you should be able to tell how they are going to split or at least as simple as how many different types or distinct groups of carbon and hydrogen are there. For this one, what we should do is, go for symmetry.

For example, if you consider a C_2 axis of rotation. So, that would make this one, this one identical and this one this one identical and here we do not have any hydrogen. If you consider ^{1}H NMR, 2 signals will be there and then if you look into ^{13}C for this molecule again with the same analogy, one should expect three different types of single resonances. So, this is the answer for this one.

Now we look into this here, we have $CH_3CH_2CH_2CH_2CH_2CH_3$.

So, CH_2, if you just look into this one it appears like only two type of signals are there, but that is not the case. This one, if you see here, it is surrounded by two methylene groups and this one is also surrounded by two methylene groups, whereas this one is surrounded by one methylene group and one methyl group and same thing is true for this one.

That means these two are of one type, and then this and this will be of another type, and this one and this one will be another type. That means ^{1}H NMR should show here three signals, Similarly the same rule applies here, ^{13}C also should show three distinct signals for this molecule.

If you are curious you can just see here it can show a quintet and this can also show a quintet identical whereas, this one will show a triplet further coupled with this one this would show a quintet here I have not plotted n m r for these things because I am asking a

different type of question here. Now, let us look into this molecule here. So, of course, this one can do like this three C_2 axis of protection one can consider this asymmetric molecule here. So, here if you see here three are there this is one type of group here and then we have another one here that means only two type of signals you can expect for this molecule here all CH_2 methylene groups are identical and all methyl groups are identical here.

So, you get two signals and in case of ^{13}C, 1 2 3; ^{13}C we expect three because one here one here and one here. So, that means, quaternary carbon methyl carbon and methylene carbon three signals are anticipated for this one then here again you can see a C_2 axis is there and this will be identical. So, this will be identical this will be identical and then this is one more here. So, this one so that means, here also you can see three here and then if you look into carbon 1 2 3 4 5 different type of carbons you can expect here. So, 1 2 3 4 5 so five different carbon elements are there here as there is a we are expecting five.

So, this is the answer for these questions. The first one will show two distinct group of hydrogen atoms and three distinct group of carbon signals and **the second** will show three hydrogen distinct multiplets and then three for different carbon atoms and in **this one** show two and three here and the last one will show three and five.

With minimum knowledge of symmetry and looking into simple operation of rotation reflection, you should be able to guess the magnetically nonequivalent or magnetically and chemically equivalent nuclei very readily and assigning and understanding would be very easy.

25. Now, one more example here, let us look into this example, here again similar problem. For this molecule also, operate C_2 axis of rotation, you can see three signals for three distinct groups. In case of ^{13}C, 1 2 3 4, 4 signals are anticipated and three hydrogen signals are expected here. Both 1 and 2 are identical

In this case again, very similar situation. We have H here and then this one here. So, that means two signals are anticipated in case of one ^1H NMR and in case of ^{13}C, three signals are expected.

In case of ^{1}H and now if you look into this here: this is distinct and this is distinct this is distinct this is distinct. So, we expect four different signals. For example, this will show two doublets this will show a singlet and this will show a singlet and then ^{13}C if you look into it 1 2 3 4 5 6 7. So, we expect seven distinct ^{13}C signals for this molecule.

26. Let us look into another set of molecules here. Same analogy here for each of the compounds.

we have to identify distinct group of carbon hydrogen atoms in their respective spectra. ^{1}H and ^{13}C. So, here these two are identical, and then we have one H and then these are CH_3 are identical. So, we can expect for this molecule 3 hydrogen signals and then if you look into carbon 1 2 3 and 4. Quaternary carbon is there, and we have another carbon and we have two carbons are identical. All methyl groups: this one is identical and then we have one. So, 1 2 3 4, 4 signals are expected. Three proton and four carbon signals.

In the second one: these two are equivalent and then these two are equivalent. So, we expect two signals and then ^{13}C, 1 2 3 we expect three signals.

Next, for this molecule here again very nice you can see C_2 axis of rotation is there. So, this one, this one are the same; this one this one are the same, and this one this one are the same. So, we are expecting here also three proton signals and if you look into ^{13}C 1 2 3 4, four signals are expected.

27. Following three compounds are put in three unlabeled vials and some information is given about their ^{13}C NMR spectra. Match the spectral futures with corresponding compounds from the list.

So, what are those compounds provided: 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene and 1,3,5-trichlorobenzene. All are trichlorobenzene, but positions of chlorine atoms are different.

I have written all three substituted trichlorobenzene here: It is 1,2,3-trichlorobenzene, this is 1,2,4-trichlorobenzene and this is 1,3,5-trichlorobenzene.

What is the question here two peaks between 125 to 140. If we just look into the different distinct carbon signals for each one, then answering these questions should not be a problem.

Now, if you look into this one of course you can see here a C_2-rotation is there. As a result, this is 1, this is 2, this is 3, and this is 4. Four signals can be expected.

In this case what would happen. So, 1 2 3 4 5 6 all 6 are different, whereas in this case we will see only 1. 2; two signals. That means, 2 peaks between 125 and 140 will be for **1,3,5-trichlorobenzene**.

Consider this one here next: six peaks between 125-140 ppm is for **1,2,4-trichlorobenzene**.

The last one is very easy for identifying, but still we can analyze. So, 4 peaks, should be **1,2,3-trichlorobenzene**.

28. Another one now: Following three compounds are put in three unlabeled vials and some information is also given about the ^{13}C NMR spectra. Match the spectral features with corresponding information provided about each one.

We have three tetrachlorobenzene derivatives, having chlorine at different positions. **1,2,3,4-tetrachlorobenzene,1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene.**

So, first let me write the structures of all, **1,2,3,4-tetrachlorobenzene,1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene**.

Let us look into the symmetry, whether any symmetry elements are there? yes we can consider here C_2 is there in this fashion, but it does not really degenerate, whether we consider like this here yes it is possible. So, this is ruled out, whereas this one is possible here. That means, basically we have three identical ones, as far as ^{13}C is concerned, three distinct carbon atoms are there.

That means in case of

1,2,3,4-tetrachlorobenzene: three distinct carbon signals

1,2,3,5-tetrachlorobenzene, four distinct carbon signals

1,2,4,5-tetrachlorobenzene. two distinct carbon signals

30. Let us look into one more example here: Predict the ^{1}H splitting pattern for the hydrogen in red color in the following compounds.

So, here this one is the red one. So, this one should show a septet here because six equivalent hydrogens are coupled, whereas this one because of one side nitrogen and other side oxygen it is not coupled to any and it will show a singlet. In this case, this will be showing a doublet. Here both are coupled to methylene, this will be a quintet and then here this will be showing a quartet and then this will show a triplet.

So, let me come up with more examples in my next lecture until then have an excellent time. Thank you.