

**Interpretative Spectroscopy**  
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**Lecture 57**  
**Problems and Solutions-6**

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. So, today again let me continue discussing some of the important problems pertinent to spectroscopic methods, how to analyze the data and how to interpret the data and elucidate the structure of unknown samples.

40. Problem 40 is here: The UV spectrum of this compound shows only end absorption. Determine the structure of the compound using the following data.

What are the data given? Mass is given, mass of parent molecular ion peak is given and also  $^1\text{H}$  NMR is given, IR spectrum is given and also  $^{13}\text{C}$  is given. With this we should find out what molecule we are referring to. First let us look into 102 here molecular mass from this one we have to try to arrive at tentative molecular formula and then we have to look into saturation and unsaturation, if there are any and we have to proceed that way. Let us begin with 102 here, we shall divide it by 13, it becomes 91 plus so 11, so that means basically  $\text{C}_7\text{H}_{18}$  and then if you go back to the spectrum here, you can see we have a very strong peak at 1740 and also we have peak around 1200. This indicates we have both CO as well as C double bond O that means carbonyl is also there and ester group is also there and that information comes with this.

Now let us add one oxygen here. To add oxygen, we have to take out one  $\text{CH}_4$  group, it becomes  $\text{C}_6\text{H}_{14}\text{O}$  since both carbonyl and ester groups are there, it has to be COO, we have to account for one more oxygen, so we will take one more  $\text{CH}_4$  to make it  $\text{C}_5\text{H}_{10}\text{O}_2$ . This is going to be the composition tallying with molecular formula here. Assuming this is correct, let us look into hydrogen deficiency index. We know the formula  $\text{C} + 1 - \frac{1}{2}\text{H}$ , because other heteroatoms are not there nitrogen as well as halogens are not there, so if you take here this is  $5 + 1 = 6 - 5$ , it gives 1. Hydrogen deficiency

is one that indicates there is only one double bond is there. In that case it should be a linear hydrocarbon.

So now we have to write the structure before we write the structure we should go back and analyze again we have two quartets are there and two triplets are there and that means if we are seeing a quartet that has to be next to a methyl group and same thing that means we have two methyl groups are there here in that case. Again, if you look into  $^{13}\text{C}$  NMR, we have 1, 2, 3, 4, 5; five distinct carbon groups are there. That means we have to think of something like this; 5 carbon atoms are there and then ester group is also there. So, we will put here something like this and then you put another one here and see whether these matches or not. If this is a correct structure, then this should show a quartet and this will show a triplet and then this will show a triplet and this will also show a quartet, but this is little bit more deshielded compared to this one here.

So, let us see whether that one is deshielded or not we can see here. This is deshielded and then this one is here and we have two triplets and then of course we look into this one. We also saw this peak as well as this peak and then we saw 5 of them and one of them carbonyl is here we can see quaternary carbon. From this one, we can say that this is the correct structure.

So, this is how we can use all available information starting from rule number 13 and then hydrogen deficiency index and then looking into any heteroatoms, looking into functional groups such as CO NH or OH and then we can arrive at the structure and interpret the data what we have obtained from actual spectrum.

41. Now let us look into another example here.

A compound composed of carbon, hydrogen & oxygen has a molecular ion at  $m/z = 90$  amu in its mass spectrum. The base peak is at  $m/z = 45$  amu. The IR spectrum shows strong absorption in the  $2840$  to  $2980\text{ cm}^{-1}$  region, and very strong absorption from  $1105$  to  $1125\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR shows two sharp signals at  $\delta = 3.40$  &  $3.55$  ppm (intensity ratio 3:2), and the  $^{13}\text{C}$  NMR also has two signals ( $\delta = 59$  &  $72$  ppm).

First let us take 90 here divide by 13, we take 78 with 6 quotient and 12 remainder. We get is  $C_6H_{18}$  here. Since one oxygen is there, let us remove  $CH_4$ , it becomes  $C_5H_{14}O$  Let us try to remove one more  $CH_4$  to add another O, it becomes  $C_4H_{10}O_2$ . When we look into these two chemical shifts: we have at 3.40 and 3.55 in 3:2 ratio. That means basically we should divide this into 6 and 4, so that means probably we have two types of hydrogen atoms and let look into hydrogen deficiency. What we get is 5 minus 5 equal to 0 ( $5-5 = 0$ ), so no unsaturation, because hydrogen index is 0.

Now we have to look into the spectrum, it has two carbon signals, H ratio is 6:4 that will give you a total of 10 hydrogen atoms. Why I have taken this one is, if you just look into the spectrum, is not given if you see both are more deshielded. If simple  $CH_3$  is there next to carbon that should come around 1 to 2. Since they are more deshielded that means they are probably next to electron negative atom here, electronegative atom is oxygen.

Now if you see  $CH_2$  is there and now they will show a singlet and then this will also show a singlet and the ratio of 3.40 and 3.55 signals is 2:3. This should be the structure of the molecule here and then this would corresponds to 90 here. This is called 1,2-dimethoxyethane.

First what we should do is, we should look into the mass from mass we can calculate like this and whatever the remainder is there add remainder to the quotient that would give you total number of hydrogen atoms present, What we got is  $C_6H_{18}$ . That corresponds to 90 and oxygen is already shown in the question, one oxygen can be added and it becomes  $C_5H_{14}O$  add one more to see what happens, it becomes  $C_4H_{10}$ . You can see it makes 3:2 ratio automatically and becomes 6 and 4. Probably it can tell you  $2CH_3$  and  $2CH_2$  units are there. We have 2 signals at 72 and 59, that means two types of carbon atoms are there and are much deshielded. As a result, we can conclude that this is the structure. All the information provided is about 1,2-dimethoxyethane. Even if I have given  $^1H$ NMR spectrum, shown here, you can see two signals are there one is at 3.4 and another one is at 3.55 for methylene, and other one is at 3.40 for methyl group.  $^{13}C$  NMR also shows two signals one is around 59 and another one is about 72 ppm. So, this proves beyond any doubt that the data

pertinent to 1, 2 dimethoxyethane is given here, the question is about identifying 1,2-dimethoxyethane.

42. Let us look into one more example here

A compound used as a moth repellent has three molecular ion peaks at  $m/z = 146$  (100%), 148 (65%) & 150 (10%) amu in its mass spectrum. A pair of smaller peaks are seen at  $m/z = 111$  (34%) & 113 (11%). The infrared spectrum shows sharp absorption just above 3000  $\text{cm}^{-1}$  region, and also at 1480  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR shows a single sharp signal at  $\delta = 7.2$  ppm, and the  $^{13}\text{C}$  NMR has two signals ( $\delta = 133$  & 130 ppm).

A compound used as a moth repellent has 3 molecular ion peaks at  $m/z$  equals 146 that is 100 percent and then 148, 65 percent, 150, 10 percent atomic mass units in its spectrum a pair of smaller peaks are seen at 111 and 113 the infrared spectrum shows sharp absorption just above 3000 and also at 1480 characteristic of an aromatic group you should remember and  $^1\text{H}$ NMR shows a sharp singlet at 7.

Molecular formula is 146 again we divide it by 13, we get quotient 11 and remainder 3. That leads to  $\text{C}_{11}\text{H}_{14}$ . Since we are referring this molecule to be moth repellent. Usually moth repellents have chlorine in them and are benzene substituents or something like that. Let us try to add one Cl by taking out  $\text{C}_2\text{H}_{11}$  to get  $\text{C}_9\text{H}_3\text{Cl}$ . Let us try to add one more chlorine atom by taking out three carbon atoms and adding one hydrogen to balance it. Then it becomes  $\text{C}_6\text{H}_4\text{Cl}_2$ .

Now let us try to find out hydrogen deficiency: 6 plus 1 = 7 minus 2 minus 1 equal to 4 ( $6+1-2-1 = 4$ ). 4 means 1 ring plus 3 double bonds. So, 3 double bonds and 1 ring fits into an aromatic group here very nicely. Now look into  $^{13}\text{C}$  signal which shows only two signals that means it is highly symmetric in nature. If it is highly symmetric and in what way we can get by putting chlorines on benzene ring to get two signals. That is only possible if you put both of them at relatively para-positions that means 1,4-dichlorobenzene or para dichlorobenzene. After putting this one let us now look into  $^1\text{H}$  signal at 7.2 yes now this is highly symmetric because you can do  $\text{C}_2$  rotation here along Cl- Cl axis and that makes all 4 hydrogen atoms chemical and magnetically equivalent.

I have also taken  $^1\text{H}$  and  $^{13}\text{C}$  NMR to compare, whatever the analysis we made, along with mass also I have taken here and you can clearly see here 4 peaks are there 146 147 148 150 relative intensities also you can see here and then in this one it shows only 1 signal around 7.45 point simulated one shows around 7.4 nevertheless it comes at 7.2 actually. So, it is here and then in case of this one  $^{13}\text{C}$  we have 2 signals here 132 and 130.

43. There is one more example here.

**Determine the structure of a compound with the formula  $\text{C}_{10}\text{H}_{12}\text{O}_2$ . In addition to the IR, and  $^1\text{H}$  NMR, tabulated data for the normal  $^{13}\text{C}$  NMR, DEPT-135, and DEPT-90 spectral data are also included.**

This gives you, information about CH proton presence. How many CH are there, how many quaternary carbon atoms are there, how many  $\text{CH}_2$  are there and how many  $\text{CH}_3$  are there. Let us look into this formula here from this formula let us find out hydrogen deficiency  $10 + 1 - 6 = 5$  ( $10 + 1 - 6 = 5$ ). 5 is the deficiency that means basically we have a ring plus 4 double bonds.

Then in this case also what we have is you can see here: There is a CO group and also an ester group.  $^1\text{H}$  NMR indicates clearly that we have two doublets and three singlets. That means they are all disconnected or in between we have oxygen atoms. Then what we have is in one  $\text{C}=\text{O}$ . Let us look into it now and see how to write the structure with this information.  $^{13}\text{C}$  NMR information is not there but  $^{13}\text{C}$  shows that many peaks are there. Now it is sufficient I believe to arrive at the structure. So, now by looking into  $^1\text{H}$  NMR you can see here see 2 doublets and 3 singlets are there.

These 3 singlets are disconnected and they do not have any nearby C-C bond at all C-C bond having hydrogen atoms. That means one can think of something like this. First let me write ring. This one should corresponds to this formula here 1 2 3 4 4 plus 2 6 this is 10 6 7 8 9 10 are there 10 and 12 O 2 this corresponds to this one this no problem. So, with this one should corresponds to this formula here 1 2 3 4 4 plus 2 6 this is 10 6 7 8 9 10 are there 10 and 12 O 2 this corresponds to this one this no problem and now these are identical and both of them will show a doublet and similarly these 2 will show a doublet

and then this will show a singlet this will show a singlet and this will show a singlet 3 singlets are there and 2 doublets are in the aromatic region.

From this one we should be able to tell the structure what it is the structure. The structure is shown, you can see the labeling is also done appropriately.

Corresponds to a this CH<sub>3</sub> here and then what we have is b corresponds to methylene group next to carbonyl and c is there methoxy group, and then d and e are 2 doublets they are coupled with the neighboring CH proton.

Now, what information this gives? As I said this information is quite vital. For example, this DEPT means **Distortionless Enhancement by Polarization Transfer experiment** is used to determine the multiplicity of carbon atoms, whether they are quaternary carbon, primary, secondary or tertiary. If you do DEPT-135 experiment, this gives you information: inverted for CH<sub>2</sub> and C group CH and CH<sub>3</sub> groups are upright. Then if you perform DEPT-90 that produces inverted C group and upright CH the CH<sub>2</sub> and CH<sub>3</sub> are null. For some nuclei with a negative gyromagnetic ratio, the DEPT experiment can provide much higher signal-to-noise ratio than the standard 1D experiment with <sup>1</sup>H decoupled NOE (Nuclear Overhauser EFFECT). So, now for comparison I have shown what are the experiments one can do in this format. So, if you see here when you take <sup>13</sup>C you get all carbon identified here. To know the nature of these carbon atoms for example, if you just take all intensities are same and you do not know which one is which one in that case you perform DEPT-45. In this experiment quaternary carbon is not seen. They disappear that indicates one information and then with DEPT-45 apart from quaternary carbon, we see all CH, CH<sub>2</sub>, CH<sub>3</sub> with DEPT-90 we see only CH whereas, in case of DEPT-135 CH and CH<sub>3</sub> are seen with CH<sub>2</sub> is inverted. So, that means, this is used to extract 3 sub spectra of CH CH<sub>2</sub> and CH<sub>3</sub> signals from a series of experiments. These experiments can be run as either DEPT-45 DEPT-90 or DEPT-135, the number corresponds to a flip angle of the <sup>1</sup>H selection pulse and that experimental manual. All these details will be there. Very easy to perform and DEPT-45 detects signals of all protonated carbons CH, CH<sub>2</sub> and CH<sub>3</sub> with the same phase, the DEPT-90 gives only CH peaks. You can see and then DEPT-135 gives signals of all protonated carbons, but CH, CH<sub>3</sub> signals are positive, whereas CH<sub>2</sub> is negative. You can

see here, the signals of quaternary carbons are absent in all DEPT spectra. By combining these, it is possible to determine multiplicity of each carbon signal. So, by doing this we can also assign the multiplicity how many hydrogen atoms are here and then eventually arriving at the structure would be rather easy very. If you have instrument in your institute or college it is a very nice learning process.

So, with this let me stop here and continue in my next lecture more problems on possibly like this as well as related to UV visible spectroscopy. Until then have an excellent time. Thank you.