Interpretative Spectroscopy

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Lecture 20

^{11}B, ^{10}B and ^{199}Hg NMR Spectroscopy

I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. Since last couple of lectures, I started discussing on NMR active nuclei other than ^{1}H and ^{13}C and in the previous one I showed you very nicely, very meticulously we can assign and interpret the spectra even if you do not know which nuclei it represents. But only thing is we should have vital information and we should analyze in a proper way. And let me continue with more such examples and this is going to be my last lecture as far as NMR is concerned and then I shall move on to UV visible spectroscopy and then IR and at the end mass spectrometry. As I have mentioned, I will come back again at the end to discuss problems related to all these spectroscopic methods. I come up with more examples of again multi nuclei NMR at the end of this lecture series.

Now let us look into ^{1}H NMR spectrum of borohydride. We all know that $NaBH_4$ where B is in a tetrahedral environment with 4 hydrogen atoms and it is anionic. I have shown here ^{1}H NMR spectrum of borohydride. The element boron, if you look into the table, I provided in my second or third lecture about all NMR active nuclei and their gyromagnetic ratio, natural abundance and also the corresponding sensitivity and nuclear spin.

So, if you consider boron it has 2 isotopes and both are NMR active. ^{10}B abundance is about 20 percent and its nuclear spin is 3 (I = 3), whereas 11 boron is 80 percent abundance and its spin is 3/2 (I = 3/2). Let us look into this spectrum and rationalize the appearance of the observed ^{1}H NMR spectrum. If you look into the first one here, we are seeing 4 lines of equal intensity and also some smaller lines here. So, 7 lines are there. Let us try to see

what it is and if you look into boron ^{10}B, I equal to 3, and if you simply use this 2nI+1 rule, it is 7. Let us put now(2x3/2 +1), that means I am considering ^{11}B here then we should get 4 lines here.

So that means we are getting 4 lines in case of ^{1}H NMR that means ^{1}H is coupled with boron ^{11}B with I equals 3/2 (I = 3/2). and it is showing 4 lines of equal intensity. This is due to $^{1}J^{11}_{BH}$ coupling, and coupling constant is in the order of 50 hertz. Now what are these 7 lines here? Now let us look into ^{10}B. In ^{10}B we have again 1 boron is there and 3 plus 1 that means 7 lines (2∗1∗3+1 = 7) should be there and this is only 20 percent. It is one-fourth of the intensity. Seven lines of equal intensity, we are seeing here, that means basically this spacing is for ^{10}B to hydrogen coupling and then this spacing is ^{11}B to hydrogen coupling. So that both are appearing here because both of them have appreciable abundance 80 percent and 20 percent that means ^{1}H NMR of boron hydride consists of coupling due to both ^{10}B which appears as 7 lines and ^{11}B which appears as quartet of 1 : 1 : 1 : 1 intensity. This is how the ^{1}H NMR spectrum of boron hydride looks like. Let us look into ^{11}B NMR spectrum of $[BH_4]^-$ anion.

Now if you consider ^{11}B NMR, you should remember the fact that boron is in tetrahedral environment with 4 equivalent hydrogen atoms as a result boron signal should be split into a quintet that is what we see here. We have quintet it is because of boron coupling with 4 equivalent hydrogen atoms. Here ^{11}B to hydrogen coupling is 64.9 Hertz and this spectrum can be obtained when we run ^{11}B NMR. So, when we run ^{10}B NMR spectrum, how it will look. It looks more or less identical except for the separation the couplings would vary, and ^{10}B NMR also shows a quintet of this intensity ratio of five lines. ^{10}B to hydrogen coupling is 27.3 Hertz, and both look identical by just looking into the spacings or couplings we should be able to distinguish between ^{11}B NMR spectrum and ^{10}B NMR spectrum. Now let us look into ^{11}B NMR spectrum of BF_3:diethyl ether. Of course, you should know that BF_3 is very reactive and we cannot store it without forming an adduct. It is unstable and then if you add BF_3 to a donor solvent such as ether or SMe_2, it forms an adduct and that can be handled easily as it is in solution. BH_3 will come as SMe_2 adduct, and BF_3 as ether

adduct is easy to handle. It comes in known molar concentration and then if you look into ^{11}B NMR spectrum, you anticipate boron to fluorine coupling and then ^{11}B NMR should consists of a quartet of 1 : 3 : 3 : 1 intensity. But how it is going to look like? It looks like a singlet that means coupling to proton or fluorine is not usually observed except in the smallest and most symmetric molecules such as $[BH_4]^-$ anion. only in case of $[BH_4]^-$, you can see coupling wherein most of the other boron compounds, whether you have fluorine on it, whether you have hydrogen on it, normally you don't see coupling, and same thing is true if you run ^{19}F NMR. ^{19}F NMR would show probably a singlet and doesn't show any coupling with boron. We have examined numerous examples of compounds having BF_2 with both ^{10}B NMR as well as ^{19}F NMR or both of them; would show only singlets. So, ^{10}B NMR has lower sensitivity and results in broader signals. So, it is always ideal to use ^{11}B NMR, unless the sample is enriched with ^{10}B due to the lower sensitivity of ^{10}B. If you want to interpret data or we want to look into the boron NMR, it is always better to go for ^{11}B NMR rather than going for ^{10}B NMR, unless the sample is enriched with ^{10}B. So now let us look into another interesting NMR active nucleus that is mercury, and mercury has two NMR active nuclei ^{199}Hg and ^{201}Hg. ^{199}Hg is about 16.84 percent abundant and its I equal to half (I = ½) and then if we look into 400-megahertz NMR, the corresponding frequency for mercury is 71.3 megahertz and the other one is ^{201}Hg that is 13.2 percent abundant and I equal to 3/2 (I = 3/2). ^{199}Hg is a low sensitivity nucleus and yields sharp signals for a wide chemical shift range, whereas ^{201}Hg is a quadrupolar low sensitivity nucleus that yields broad signals and ^{199}Hg NMR used for the study of mercury compounds their structure dynamics and conformation. It is also used for biological binding studies by using its relaxation effects. Once again whether we are looking into ^{199}Hg or ^{201}Hg , the standard used is dimethyl mercury. So dimethyl mercury is set as zero and then the chemical shift range can be thousand to -3000. For mercury iodide, comes around -3000 and mercury nitro compound comes between -2000 to -3000 and dibromo mercury shows around -2000 and between -1000 to -2000 for mercury chloride. Of course, here you can see the organo mercury compounds and organo mercurial compounds come in the range that is shown here. Let us look into some examples of compounds containing mercury, one such example is dimethyl mercury, and if you look into ^{199}Hg NMR here, you can see six hydrogen atoms are there. So CH_3, CH_3 so here six hydrogen atoms are equally coupled to

mercury and as a result what we are getting is a septet here. So, ^{199}Hg to hydrogen coupling is of 100.9 Hertz here. Then when we look into ^{1}H NMR spectrum of dimethyl mercury, we get one signal here. This is for NMR inactive and then since we have a small percentage of ^{199}Hg is there. It will also show a satellite peak here. Here the mercury hydrogen coupling is 109 Hertz. This should be same as this one here. So, that means ^{1}H NMR spectrum consists of a singlet with mercury coupling satellites with a mercury hydrogen coupling of 109 Hertz, whereas ^{199}Hg NMR consists of seven lines, the septet is because of coupling with hydrogen atom so now let us look into ^{13}C NMR of dimethyl mercury and again here you can expect one broad signal having mercury satellites. $^{1}\mathbf{J}$ ^{199}Hg to ^{13}C coupling is 686.2 Hertz. We have another interesting molecule. we have dialkenyl mercury compound. We have here three different types of fluorine atoms on each carbon, you can distinguish, these two are identical in the red, and then we have in the green are identical and then these two are identical that means they are equally coupling to mercury, so that means, first these two bond apart fluorine atoms will split mercury into triplet, so this one is $^{2}J_{HgF}$ coupling. Now we will come to this one, this will be split into triplet again. So, I have given in the color here. So, if you see, one two three bond coupling to mercury, now we have blue ones; there also one two three coupling. So, they are further splitting this into triplet here. So, if you see here, this can be called as triplet of triplets of triplets. If you want to spell out this. How we should say whatever the splitting pattern you have to start from the beginning that should come first because triplet of triplets of triplets, this is how we should pronounce the spectrum, and this is how it is going to look like, and of course you can also distinguish here the various couplings. So, this is a very interesting structure here. NMR spectrum here for mercury, so triplet of triplets of triplets. let us look into one more interesting spectrum, here look into here, one of the fluorine is replaced by CF_3 group, that means basically to begin with very similar to what we had earlier. These two would couple together to give a triplet and then next these two would couple to split this triplet into triplets, and now the CF_3 group, we have six of them, six equivalents are there. So, six equivalent means, if you again go with the 2nI +1 rule (2∗6∗1/2+1 = 7) that means each of these triplet lines will be further split into seven lines. So, something like this. So, that means, this one we can call it as triplet of triplets of septets. So, this how the spectrum looks like this is a triplet of triplets of septets. I think that's enough about mercury NMR

and in case if we have some examples where interpretation is a problem you can always show it to me so that I can interpret and give the information back to you. Let us look into one more example here. Trifluorophenyl substituted boron here and this is a ^{19}F NMR spectrum, and if you look into ^{19}F NMR spectrum and by just looking into it you can conclude that these two are equivalent or ortho fluorine atoms are equivalent and then we have meta fluorine atoms are another set and then we have another set in 1 : 2 : 2 ratio that means we can see three different types of fluorine atoms. They can also couple with boron or hydrogen, as a result, they show a multiplet and do not have a resolved spectrum here, but nevertheless by looking into those things, you should be able to identify three different types of fluorine environments in this molecule. So now let us look into one more example. This is about Pb, lead also has several naturally occurring isotopes including ^{204}Pb, 1.5 percent natural abundance and ^{206}Pb, 24 percent abundance and also, we have ^{207}Pb 22 percent abundance and also, we have ^{208}Pb, 52 percent abundance. Of these isotopes, only ^{207}Pb has non-zero nuclear spin of I equal to half (I = ½). This is NMR active, that means, if you have any lead compound like tetra methyl lead or tetra ethyl lead, certainly we can run ^{207}Pb NMR to know its chemical shift environment and what would you expect to observe for the ^{1}H NMR spectrum of tetra methyl lead. Given, the $^{2}J_{PbH}$ coupling is 60 hertz that means the value is given for PbH and if you just look into tetra methyl lead, the data provided is two bond coupling of 60 hertz. How the ^{1}H NMR spectrum would look like in case of tetra methyl lead. So, let us draw and you should remember the fact that ^{207}Pb abundance is only 22 percent. So, if it is 22 percent then the 78 percent should be with I equal to zero (I = 0), NMR inactive lead. So that would show a singlet something like this. That means out of hundred molecules of tetra methyl lead about 78 molecules do not have NMR active lead, as a result that would appear as a singlet here, whereas 22 percent of ^{207}Pb would split hydrogen signal into a doublet something like this here. Then this would be 11 percent and this would be 11 percent and this is 78 percent and then this coupling is 60 hertz; this is what the information is given. This is how the ^{1}H NMR spectrum of tetra methyl lead. So, this is all about lead NMR, and of course today I discussed about ^{10}B, ^{11}B NMR and ^{199}Hg NMR and also how boron interaction would take place in sodium borohydride to give a quartet for ^{11}B coupling and also septet for ^{10}B with I equal to 3 (I = 3) and 11 boron with I equal to 3/2 (I = 3/2). In case of boron compounds,

you should remember: if the molecule is not symmetric probably you don't see boron-fluorine coupling or boron hydrogen coupling, whereas in case of symmetric molecules such as BH_4, we saw very nicely splitting of boron by hydrogen as well as hydrogen by boron and also, we could see in ^{1}H NMR spectrum of boron hydride coupling of both ^{11}B and ^{10}B.

So, with this let me stop here and continue in my next lecture about a new spectroscopy topic, that is UV visible spectroscopy. Until then have an excellent time reading interpretative spectroscopy. Thank you so much.