Interpretative Spectroscopy

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Lecture 13

Multinuclear NMR Spectroscopy-2

Hello everyone, once again I welcome you all to MSB lecture series on interpretative spectroscopy and today let me discuss again on ^{31}P NMR spectroscopy. In my previous lecture I gave you very good examples of identifying different isomers of square planar complex and also a squarepyramidal complexes and also how to distinguish if the coordination number is 5 for a d^8 system. Two possibilities are there in having an appropriate geometry that is square pyramidal or trigonal pyramidal geometry and how the geometrical changes can happen with temperature, we saw in case of rhodium complex having four trimethyl phosphine [$(CH_3)_3P$] and methyl composition in its coordination sphere. Let me continue with more interesting examples in this lecture. Now I am giving another interesting molecule here. Let us try to analyze the spectra given. This spectrum is of 195 platinum (^{195}Pt) NMR. In this spectrum, if you see, we have two triplets of equal intensity. Then if you look into the structure here, we have platinum, platinum is directly attached to ^{15}N that means here enriched molecule with ^{15}N and we have another molecule here isocyanate where we have carbon to nitrogen triple bond and we have CH_2 and it seems hydrogen is not interfering in this ^{195}Pt NMR. So let us try to analyze, and first thing we should look into is this is enriched with ^{15}N. We know that I equal to half (I = ½). If it is interacting with platinum which is one bond apart, it should split the platinum signal into a doublet and this should be $^1J_{Pt}{}^{15}{}_N$ coupling.

Now we have each line is split into a triplet of equal intensity. Here if triplet of equal intensity means we should think of nuclear spin value something else, and of course, in close vicinity, we have ^{13}C carbon, but carbon does not split something like this here because ^{13}C has I equal to half (I = ½). Also, its abundance is only 1%, there is a possibility of seeing satellites but on the other hand here we have ^{14}N and ^{14}N we know that I equal to 1 (I = 1). Now if it is splitting this one, we can use 2nI + 1 rule. Only one ^{14}N is there and then its spin is 1 plus 1 so it will

be 3. We will have 3 peaks and when I equal to 1(I =1), and triplet is there. Intensity ratio is 1 is to 1 is to 1 (1:1:1). So, in this case, it should split something like this. Unlike the splitting with nucleus with I equal to half (I = ½), where intensity ratio is 1 is to 2 is to 1 (1:2:1). Here it is 1 is to 1 is to 1 (1:1:1). and then if you assume this is ^2J this is $^2J_{PtN}$ coupling, then it should appear something like this. We can correlate this one. this is $^1J Pt^{15}N$ and then if you take any of this separation this is $^2J Pt^{14}N$. This is how although it appears complicated when you understand, it becomes very easy. So, this is 195Platinum (^{195}Pt) NMR. This involves both $^1J_{Pt}{}^{15}_N$ coupling as well as $^2J_{Pt}{}^{14}_N$. Normally we do not see ^{14}N coupling and in case if we get something like this, interpretation would be rather easy. So, this is a typical ^{195}Pt NMR spectrum and again when we look into ^{195}Pt here it is very similar to carrying out ^{13}C NMR measurement. Now I have given a set of chemical shifts or spectra here and then write the appropriate structures and match the corresponding ^{31}P NMR spectrum for the following inorganic cages and explain. So that means 4 spectra are given and I would be providing 4 molecules here. For each molecule now you have to interpret and identify which molecule has which spectrum here. Then if you look into P_4 it is a tetrahedral molecule with each phosphorus having 3 bonds connected to each other and in this, all the phosphorus atoms are identical. They are chemically and magnetically equivalent. As a result, one should expect a single resonance in its ^{31}P NMR spectrum. So here: one: it could be this one, one here, it can be this one or it can be this one here. Come back to that one and now.

Let us look into this molecule and when we react P_4 with excess of oxygen and we can get P_4O_{10}. In the same way, if we react white phosphorus with excess of sulfur we can get the analogous sulfide compound, that is P_4S_{10}, and here all phosphorus atoms are pentavalent and tetra coordinated having one phosphorus to sulfur double bond and three phosphorus to sulfur single bonds. As a result, all of them are chemically and magnetically equivalent and the molecule is very symmetric. As a result, we also expect for this one to show one peak. It could be this one or this one. And next let us look into this molecule here. In this molecule two phosphorus are in pentavalent state and two phosphorus are in trivalent state. That means we have two different types of phosphorus atoms. These two are identical and these two are identical. These two phosphorus atoms are equidistance from trivalent phosphorus. Here trivalent phosphorus, that means this two phosphorus can be coupled with trivalent phosphorus to give a triplet, and similarly, pentavalent phosphorus also can couple with two trivalent phosphorus to give a triplet that means the spectrum should have two triplets. Yes, these two triplets and this corresponding to this molecule here.

Now if you look into fourth molecule here, in case of fourth molecule, one of the four phosphorus atoms have three P—S bonds, and others keep P—P bonds intact. Just by looking into the molecule, you should be able to tell that we have two different types of phosphorus atoms in a ratio of 1:3and this is one type, if I say this is A and these are all B or if I say a this can be X. I think it is appropriate to use letters farthest, because one is very different from the rest of three. So, if I put A here there should be X here. That means we are talking about AX_3 spin system. AX_3 spin system A is coupled with 3X to give a quartet delta-A (δ_A) if you look into it, it would be something like this quartet and if we look into delta-X so this will be a doublet. So, these 3 are identical; they split with A to give a doublet and then A will be split by 3X to give a quartet. So, we have here, so this is for P4. So that means basically when we take white phosphorus and react with excess of sulfur, and if we abruptly stop this reaction, it is likely that we can get all these products along with unreacted white phosphorus also. In that case, without any problem we should be able to distinguish. Then how to distinguish between this one and this one. For that one, we have to take the spectrum of pure white phosphorus then we should be able to identify or we have to do excess reaction for this isolated molecule you have taken and then we should be able to distinguish between this one and this one. So, this is how when we get more than one type of product in a reaction mixture and if we have phosphorus in it, it is very easy to distinguish and identify the corresponding products. So here that is the explanation I have given here. This one, you can call it as A_2X_2 spin system and this is AX_3 spin system. Now let us look into the NMR spectrum of PF_5. Both ^{31}P NMR and ^{19}F NMR. PF_5, we all know that it is highly fluxional molecule and it is trigonal bipyramidal and because of fluxionality what happens, we may not be able to distinguish axial fluorine with equatorial ones. So, at room temperature, if you record ^{31}P NMR, all are identical as I said we cannot distinguish between equatorial and axial ones. As a result, all five would be coupled with phosphorus to give a sextet; it should give six lines and it should appear as something like this, and this is the ^{31}P NMR spectrum. Now if you look into fluorine NMR, again, you cannot distinguish between axial and equatorial. As a result, you will see a single resonance for all the fluorine atoms. But that is coupled with phosphorus so it appears as a simple doublet something like this, but if the molecule is static, what would happen? The next question is: if the molecule is static then let us look into ^{19}F spectrum. If the molecule is static, then this is axial, and this is equatorial. So let us say: There are two possibilities: first it can interact with the axial ones or it can also interact with equatorial ones that means unless we know the magnitude of the coupling constant of phosphorus with equatorial

fluorine and axial fluorine we may not be able to tell it, but on the other hand, if the molecule is frozen, say, minus 80 degree centigrade (-80 °C), we assume that all dynamic process comes to an halt and it is static so that there is no Berry pseudo rotation to exchange axial ones with equatorial ones. In that case, if we take record the spectrum, we should be able to tell simply by looking into the spectral pattern, whether the fluorine to phosphorus axial is larger in magnitude or phosphorus to equatorial fluorine coupling is maximum. So, let us look into both the cases here. First let us assume $^1J_{PFaxial}$ is greater than $^1J_{PFequatorial}$. So now first what would happen is the phosphorus signal will be split into a triplet here and then each line will be split into a quartet, so something like this, that means it is basically a triplet of quartets. We will see a triplet of quartets. On the other hand, if we see $J_{PFequatorial}$ is greater than $J_{PFaxial}$. First, they split this into a quartet and then each one will be split into a triplet here because of two axial ones and this one is J_{PFequ} and now each one will be split into a triplet so this coupling will be here, axial. In this case it appears something like this. So now by simply looking into the spectrum we should be able to tell whether magnitude of phosphorus to fluorine axial one is larger or phosphorus to fluorine equatorial is larger. So, this one will be something like this. This is a triplet, something like this. It shows of course 1:3:3:1 ratio is maintained and overall 1:2:1 is maintained. So this is how we can sketch NMR spectrum after looking into the coupling tree. We call this as coupling tree. Now I have three more examples here. Sketch the ^{19}F NMR spectrum of PF_5 that I have already done. Sketch the respective NMR spectrum for the following compounds showing all reasonable couplings. Here let us take one at a time and again if you look into first molecule, here we have a square planar complex and in this one again we have two isotopes: ^{196}Pt with I equal to 0 (I = 0) that is 66% and then ^{195}Pt I equal to half (I = ½) with 34% abundance. Now we have one phosphorus that is directly connected to phosphorus and then we have phosphine imine. We have another phosphorus this is pentavalent and this if you say A, this one is X and also this is M so we are talking about AMX spin system. AMX spin system differs little bit in the sense M is not 100% abundant, whereas in this case we can see very identical but instead of phenyl groups and phosphorus we have fluorine and another NMR active nuclei. Here we have P=S that means basically you can take this is one type, this is another type, and this is another type so that means we have in case of ^{31}P NMR, we can anticipate two signals and each signal will be split in a different way and then if you just look into this case, it is very interesting and if you just look into ^{14}N NMR, let us say ^{14}N NMR what would happen is hydrogen is also one bond apart and phosphorus is also one bond apart in this case. We have to see different situation here. So i)

is nitrogen to hydrogen coupling is larger than nitrogen to phosphorus coupling; on the other hand ii) nitrogen to phosphorus coupling is larger than nitrogen to hydrogen coupling, and the third one is iii) both the couplings are identical. That means, if somebody asked you to sketch the ^{14}N NMR spectrum of this molecule, without knowing the difference in the magnitude of these couplings, we should be able to sketch all three possible ones and after plotting or recording actual NMR spectrum we can compare and we can conclude what actually it is. So, let us take one at a time now.

Let us look into ^{195}Pt NMR spectrum of this molecule. Here first, this platinum is coupled with phosphorus to give a doublet, and each line in the doublet will be further split into another doublet because of $^2J_{PtP}$ coupling. That is shown here, and this corresponds to $^2J_{PtP}$ coupling, and this corresponds to $^1J_{PtP}$ coupling. So, it shows a doublet of doublet. Now I would come back to phosphorus NMR.

Now let's look into this molecule here. A PP bonded compound with one of the phosphorus is oxidized with selenium, so ^{77}Se is about six percent I think with 7.6% natural abundance and I equal to half (I = ½). Rest is ^{76}Se which is NMR inactive. But when you are looking into ^{77}Se NMR, first this will be coupled with doubly bonded phosphorus and this coupling comes anywhere between 780 to 1200 Hertz. First it splits by this one and then, we have two bond coupling also, that will split each line into another doublet, and this coupling magnitude is much lower. It can be anywhere between up to 50 Hertz or 100 Hertz. So, you can see it also appears as a doublet of doublet.

Let us look into the platinum compound and phosphorus NMR here. In ^{31}P NMR, if you just look into 66% NMR inactive molecules as ^{196}Pt is inactive with I = zero (I = 0). What we get is a doublet here and a doublet here this is simply $^2J_{PP}$ coupling, and this is $^2J_{PP}$ coupling so let us say this is P_O and then this is P_N something like this, we can denote. And now what happens? this accounts for 66% of molecules, 66 corresponds to ^{196}Pt bound, but how about ^{195}Pt bound; they will be split further so something like this a doublet and then doublet something like this, now this coupling and this coupling. So, this is for the $^1J_{PtPO}$ coupling and this is $^1J_{PtPN}$ coupling. So, this can be anywhere between 2500, it can go to as high as 7000 Hertz. So we should be able to again draw or sketch the NMR spectrum for this molecule here, and if we sketch phosphorus NMR, here for this one again, both are different, AX system; we can get something like this. and now this selenium is also there so what happens? the one that is say if it is selenium bound and this is with lone pair. This one will be split and it will be splitting

something like this and then we will be having satellites here and then this coupling what we call it as $^1J_{PSC}$ coupling here and whereas this one it is less likely to show. Even if it shows, the coupling magnitude is very small. Let us say, if it is there, it is something like this, and then in this case it will be $^2J_{PSC}$ coupling. So, once we know the relationship and what is the natural abundance, we should be able to sketch appropriate NMR spectrum, no matter which nuclei we are talking about.

Let me stop here and come up with a few more interesting molecules in my next lecture. I showed you here a rhodium compound let me discuss NMR spectrum of that rhodium compound in my next lecture. Until then have an excellent time, thank you.