Interpretative Spectroscopy

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Lecture 12

Multinuclear NMR Spectroscopy-1

Hello everyone, it is a pleasure to welcome you all once again to MSB lecture series on interpretative spectroscopy. In my last couple of lectures, I started discussion on ^{13}C NMR spectroscopy. So, let me continue from where I had stopped, and let us look into molecules having more than one NMR active nuclei. For example, if you look into phosphorus compounds, we can have ^{19}F, fluorine, we can have ^{1}H and of course, we can have ^{13}C. Let us try to look into more interesting molecules and try to interpret the data obtained from different NMR nuclei. So, one such examples I am going to show you here, and look into this phosphorous compound here.

We have on phosphorous, one fluorine is there and one H is there, and one OH group is there and also, I have displayed ^{1}H NMR spectrum, ^{19}F NMR spectrum and also ^{31}P NMR spectrum. So, let us see how one can split the lines to see multiplets are okay or not. For example, if you just look into ^{1}H NMR, there are two types of hydrogen atoms. One is OH and other one is directly attached to phosphorus H, and we know that phosphorus to fluorine and phosphorus to hydrogen which are one bond apart, show huge or large amount of coupling constant and they come in the order of 800 to 900 and sometime up to 1200 hertz (Hz).

In this example, if you just look into the OH signal, it comes around 14, it is pretty deshielded and then when you look into hydrogen, now hydrogen can split by two ways. One is with one bond separated phosphorus that splits into a doublet and then each line in the doublet will be further split into doublets because of two bond coupling with fluorine.

So, let us ignore this one time being, let us focus our attention on signal of this directly phosphorus bound hydrogen. First it shows a doublet and this we call it as $^{1}J_{P\text{-}H}$ and of course magnitude is also given here. It is 780 hertz (Hz), then it will be coupled with fluorine.

So, this will be a doublet and this is 115 hertz (Hz). So, this is again 115 hertz (Hz), this is $^{2}J_{FH}$ coupling. So, now the spectrum should look like, so you can see here this is the spectrum. So, this is how you can interpret the splitting and now let us look into ^{19}F here. ^{19}F when you consider again, this is first coupled to phosphorus and then it will be coupled to hydrogen and it is very similar to what we saw in case of ^{1}H NMR signal for this one.

This distance is called $^{1}J_{PF}$, $^{1}J_{PF}$ is 1030 hertz (Hz) here, and then each line is further split because of ^{2}J a coupling here, this is 115 hertz (Hz). So, this is also a doublet of doublet. So, phosphorus NMR we can focus our attention again. First it will be coupled to PF because here PF coupling is much larger. So, it first splits into doublet and here this is the coupling, this is 1030 hertz (Hz) and then each line in similar fashion, will be split by hydrogen and this is $^{1}J_{PH}$ coupling, this is 780 hertz (Hz). So, all of them look identical except if you omit this portion all of them look identical doublet of doublets, because they all have two couplings with one bond and two bond coupling.

So, this is how you can interpret data very easily and you must have understood now how easy it is, to interpret data obtained from multi nuclear NMR spectra. Let us look into more such examples here of course, here I have shown you. So, it is doublet of doublet here first it splits by fluorine $^{1}J_{PF}$ and then each line will be split into further two lines because of PH coupling, PH coupling this is 1030 and then this is 780 hertz (Hz). So, it appears like this. Now, I have displayed all of them you, can clearly see here.

Now, let us move on to another example, where instead of one F we have two F, and then instead of OH we have a H, here and again we can interpret data in a similar fashion. First let us take up ^{1}H NMR, if you take first, it will be split into a doublet this is $^{1}J_{PH}$ and $^{1}J_{PH}$

is about 880 hertz (Hz) here, given. So, now, each line will be split into a triplet because we have two chemically and magnetically equivalent fluorine atoms and they are two bonds apart from hydrogen. So, they split this one into triplet; that means basically it happens something like this and this spacing is $^{2}J_{FH}$ coupling and this is in the order of 115 hertz (Hz) and the spectrum should look like. So, this is 1 : 2 : 1 ratio you should remember from Pascal or if you have forgotten, I can show you again.

So, we have two of them: one is like this, one will be like this and so this ratio is 1 : 2 :1. So, what you get is, this is what I have shown here. So, it is very easy to interpret: This is about ^{1}H NMR spectrum. Now let us look into ^{19}F NMR spectrum, here ^{19}F, if you see, these two fluorine atoms are equivalent. So, they will show one chemical shift first, they will be coupled with phosphorus to show a doublet and each line in the doublet will be further split into doublet because of $^{2}J_{PH}$ coupling, and as a result, what we get is a doublet of doublet and this $^{1}J_{PF}$ value is given $^{1}J_{PF}$ is 1110 hertz (Hz) and then here this is FH coupling this is about 115 hertz (Hz).

So, this is again a doublet of doublets. So, what is left is now ^{31}P NMR. So, ^{31}P NMR if you see here, we saw from the previous ^{19}F NMR that PF coupling is larger compared to PH coupling, as a result first P signal is split into triplet, and then each line will be split by the same $^{1}J_{PF}$ coupling the magnitude of that one is little less. So, it comes second first we will take something like this. So, this spacing is same as this spacing this is our $^{1}J_{PF}$ and this is 1110 hertz (Hz), and now each line is split into a doublet here.

So, now all are identical, these spacings are identical. This is $^{1}J_{PF}$; this is 880 hertz (Hz), but the spectrum should have looked something like, but if you just see, there is little bit of overlapping, it appears for this one, and these two are one and for this one little bit overlapping is there, because what happens if you see the difference is much less here. As a result, what happens? Little bit it comes here and it comes here little bit and same thing; it comes little bit here and it little bit here as a result what happened the spacing does not

look like uniform. So, now it appears like this, so but still we should be able to interpret the data to understand the splitting pattern. So, you can see that one, that is PH coupling.

So, now let us look into two examples given here. Two isomers of a square planar complex are shown here. We have on platinum two PMe_3 groups and one bromine and one chlorine [$Pt(PMe_3)_2BrCl$)] are there, and you know that square planar complexes of the type MA_2B_2 or MA_2BC. So, they can show isomerization and when you look into isomerization, two type of isomers are possible. One is cis, one is trans here and then how to distinguish them.

For example, I made these compounds in a particular reaction in that one, I do not know which isomer I got, or I must have got both the isomers. Then how to interpret the data. Just if you just look into this trans compound, here trans compound, we can do C_2 axis rotation, as a result what happens, these two are identical indistinguishable, whereas here you cannot do that one. So, if you do the C_2 axis rotation, Br goes here and Cl goes here. So, it does not have C_2 axis of rotation, and either in this direction or in this direction. So, here two phosphorus are chemically equivalent, but they are not magnetically equivalent, as a result and of course, even chemically as they are not equivalent, because one is cis to chlorine, one is trans to bromine, otherwise this one is cis to bromine and trans to chlorine as a result both are different. So, both of them show separate signals and then we know that we have two isotopes: ^{195}Pt, ^{196}Pt . ^{195}Pt is roughly 34 percent NMR active, with I equal to half (I = ½), and then this is 66 percent is NMR inactive, with I = 0.

So, that means basically if I take any of these isomers 100 molecules, out of 100 molecules 66 molecules do not show any interaction with platinum, because of ^{196}Pt which is having I equal to 0 (I = 0), and then if you consider the other 34 percent, they will be interacting with ^{195}Pt with I equal to half (I = ½), that can split the phosphorus signal. So, first let us consider this one, we get a singlet like this for 66 percent of that one, no coupling with platinum, whereas this one will split into a doublet here where it is splitting into a doublet something like this they will be coming and if this is 66 percent this will be 17 percent intensity, this will be 17 percent. So, something like this and then this separation we call it as $^1J_{PtP}$. So, this is how a trans compound would look like, but on the other hand, when we

look into cis, we will get two signals here. Two signals and also because of difference in their chemical and magnetic behavior, they split each one into a doublet.

So, that means basically you get a doublet here and you get a doublet here one is for this one is for this one. This platinum also splits each into further a doublet, here, something like this, and this one might come here and something like this will be there very similar to here and this. Spacing is same as this spacing and then here this spacing is same as this spacing. So, here if you are saying A and B this is $^{\delta}P_A$ and this is $^{\delta}P_B$ and then if you take here this is $^{1}J_{PtPA}$ and then if I take this one is here. So, for example, the center of the midline if I take, this is $^{1}J_{PtPB}$. So, it is basically having two sets of this, that is it, because they have again coupling between them. So, each line will be split into a doublet.

So, this is how we can interpret and the moment we look into spectrum we should be able to tell whether we have obtained cis isomer or trans isomer or both of them are present in certain stoichiometric ratio by looking into the intensity we should be able to tell whether the cis is 75 percent, trans is 25 percent or vice versa. So, this gives some idea about the type of isomers we have obtained and also how the spectrum looks like. So, it is very easy to distinguish. On the other hand when we carried out this reaction, we do not know whether we got cis isomer or trans isomer. If the spectrum is provided, then we should be able to tell which isomer is present or there is a possibility of the presence of both isomers in different stoichiometric ratio. I have another interesting molecule here. ^{31}P NMR spectrum of tetrakis(trimethylphosphine)(methyl)rhodium $[Rh(P(CH_3)_3)_4(CH_3)]$ compound shows some sort of a flexionality at room temperature. It shows a doublet at -80°C or it shows two signals one is doublet of doublets and another one is quartet ofdoublets.

So, how that happens? First we should look into the molecule and how many ligands are there and of course, by looking into the molecule, we should be able to tell that it is rhodium(I). Let me write the possible structures. First let me write square pyramidal geometries; all possible. So, this is one possibility where all phosphines are in the plane and methyl in the axial position. So, this is another possibility. I do not think I should be

able to write any more isomers for square pyramidal geometry. Here only two are possible. Now, another possibility is trigonal bipyramidal.

So, here let me put two phosphines the axial position and two in the equatorial plane and then one methyl group here or other possibilities one methyl group is here one phosphine is here. So, these so now, these are the possibilities I do not think any other isomeric forms are possible for this one. At room temperature what we are getting is a simple doublet. Why we are getting a simple doublet, here we should remember ^{103}Rh is NMR active it is 100 percent abundant and I equal to half (I = 1/2) and then phosphorus to rhodium coupling constant would be anywhere between 160 to 300 hertz (Hz). As a result, in this case, if I write it couples. So, all these phosphorus atoms are equivalent and they couple with rhodium to give a doublet here. That means, if the correct structure is for this one, this is the doublet.

So, at room temperature it shows a doublet means the structure is something like this, where four trimethyl phosphine groups are in the plane and one methyl group in the axial position. So, now, let us look into doublet of doublets and quartet of doublets, here if you just look into this structure, here in this structure, one is axial and this is you know making cis relationship with remaining three. So, first let us say this will couple with this one to give a doublet, this one will couple with this one to doublet, and each line will be a quartet. Same thing is true in case of this also, if you see here. So, this is coupled with rhodium to give a doublet and each line in the doublet is split into one two three.

So, quartet here. So, that means, two possibilities are there, whether it has this structure or whether he has this structure that we have to analyze now first let us look into these three in the plane when you look into these three in the plane what actually happens is. So, this one is trans to this one and these two are trans to each other. As a result, what happens this may not be a right structure for interpretation of this data provided here quartet of doublets and probably here. These three are identical. So, these three would couple equally to rhodium and then they couple with this one to show a doublet. So, the doublet is here.

These three in the equatorial plane would couple with rhodium to give a doublet and then this will be split again into doublet here. So, this is $^{1}J_{RhP}$ coupling and then this is PP coupling $^{2}J_{PP}$ coupling.

So, yes this is a doublet of doublet. This is fine. These are taken care and now this will be split into this doublet first and then it will first split by rhodium to give a doublet and each line in the doublet will be a quartet here, and then this is $^{2}J_{PP}$ and then this is $^{1}J_{RhP}$. So, that means the axial one, this is for axial one, then this is for equatorial one. Now, we can say at room temperature, this molecule exists in square pyramidal geometry, but at -80°C, this turns into trigonal bipyramidal geometry having three phosphines in the equatorial plane and one being axial. So, this explains that way we can also understand the fluxionality and the type of geometrical changes that happens with temperature. So, here ^{31}P NMR comes very handy in understanding both the geometry and also the position of ligands in the coordination sphere.

With this, let me stop here and continue with more interesting examples in my next lecture. Thank you.