Interpretative Spectroscopy

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Lecture 10

Introduction to ^{31}P NMR Spectroscopy

Hello everyone, I once again welcome you all to MSB lecture series on interpretive spectroscopy. This is the tenth lecture in the series. In my previous lecture, I was discussing about ^{13}C NMR spectra and related aspects and how one can compare the data obtained from ^{1}H NMR with ^{13}C and how to simplify ^{13}C if you have large number of hydrogen atoms, we use decoupling system. So, let me continue from where I had stopped. Just if you recall the spectra I showed in my last lecture, you can see here ^{13}C NMR spectra is recorded both with coupling and without coupling. This is without coupling I would say ^{13}C like this.

Once if you write in the flower bracket any nuclei next to the one we are looking into that indicates any signal due to this one is decoupled and this one is coupled one. So, in the coupled one you anticipate interaction of carbon with adjacent hydrogen atoms. For example, here when carbon interacts with 3, we should get a quadrate we are seeing here and then again, this one is also this carbon also coupled with these three and it will show another quadrate here and then this one methylene is split by two hydrogen atoms. So, we are getting three here.

If you are not understanding how this is giving for example, here we can use simply 2nI plus 1 (2nI +1) rule here. So, here carbon is attached to three hydrogen atoms to two into three and its spin is half (I =1/2). So, it gives four lines. This is how you can calculate. So, we are seeing four lines and in case of this one also we are seeing four lines whereas in case of methylene we are seeing three lines and of course here what happens we have one

two three four different type of carbon nuclei are there as a result we are seeing one two three four.

So, this is much better. This is simplified one. In case if you want to have further information to see how it is interacting and one can always record coupled spectrum whether it is ^{13}C or whether it is phosphorous NMR or it is chlorine NMR we can always record coupled as well as decoupled ones. One example is shown here. We have a para position.

We have fluoro group there. So, parafluorotoluene it is, and if you just look into this molecule here, this-one and this-one are identical and this-one and this-one are identical. This is unique. This is unique and this is unique. That means one two three four five peaks should be there.

So, we have here one two three four five signals are there and then it is a simple but fluorine is also there. It is likely that fluorine can couple strongly with this carbon atom here this carbon atom here and then it can weakly couple with these two as well but here it may not show any coupling because one two three bond coupling. Let me see how it looks like. Yes, you can see here the one with larger coupling what we see here this is due to this one bond carbon fluorine coupling whereas these two will be coupled with this one that is little long range you can see here and then these two are coupled weakly and that can be seen here and then this doesn't show any coupling it comes here and this one is coming here. So, that means basically coupling also helps in understanding the position of signals in a given spectrum.

Now, I am presenting another interesting molecule here. You can see dichlorotrimethylsilyl methane here and if we look into ^{13}C NMR spectrum we are expecting two signals here one is for this methane carbon and then other one is methyl group present on silicon. So, here and simply by looking into the coupled spectrum the C

^{13}C this one will couple with H_2 show a doublet and then this carbon here all three are equivalent as a result we can anticipate only one carbon signal in each carbon signal. So, you can see the coupling with three protons. So, it will show appear as a quadrate, but if we look into the fine spectrum of this one of expanding this quadrate on expanding each line would be consists of a septate and each septate is again each line is a doublet and similarly if we look into the signals here in the doublet each signal is consists of ten lines here.

So, it is interesting to analyze how these ten lines are coming here and how each one is a separate of doublets how it is appearing here. You can see here first I have expanded version of this one I am showing here in why each line is showing ten lines here and of course, if I just write the structure here. So, first this carbon will couple with hydrogen to give a doublet certain larger coupling one can anticipate now this carbon is coupled with one two three bond coupling three bond coupling with nine hydrogen atoms are there nine hydrogen atoms are there if I just again use this 2nI + 1 rule here 2 into we have nine So, ten lines, you can expect ten lines (2∗9∗1/2+1 =10). that is what we are seeing here. That means you can also see $^1J_{CH}$ coupling plus we are seeing 1 2 3 3 J_{CH} coupling.

So, first it will appear as a doublet and each line will be split into ten lines. So, you can see ten lines here. So, this is how you can understand the complex pattern, although it appears like a doublet, after expanding you can see the fine splitting here showing both ^1J as well as ^3J coupling with hydrogen atoms. Now, let us look into the quartet here. In the quartet, it is very interesting, let us just look into trimethylsilyl group here.

So, once when we are considering one of the signals here, ^{13}C others may be 12 not necessarily there will be 13 in this case what happens first it will split with this one into a quartet and then these two are non-equivalent. They split protons into a septet. The same thing happens in all cases after that one you can see again ^3J coupling this one will be coupled with this hydrogen 1 1 2 3 coupling. So, ^3J coupling is also anticipated, only one is there, each one will be split into a doublet. So, you can see now this is how a quartet

after expansion appears like septets of doublets. You can see here. Each quartet is split into 7 lines and then each line in the septet is further split into a doublet because of $^{3}J_{CH}$ coupling and then eventually if you just look into it, appears like this. It is very simple to understand, if we expand we get the fine spectrum. And let us look into another example here and in this molecule all are very different as a result we can anticipate 6 carbon atoms in the aromatic region and all the 6 carbon atoms are shown here one is here, two is here and 3 4 5 6 are there and now if we just look into one, one is split into a doublet because this one is about one two bond coupling this is due to two bond carbon fluorine coupling and then two is directly attached to fluorine.

So, we can anticipate larger coupling, as a result, it is split further. This is $^{1}J_{CF}$, whereas this portion is $^{2}J_{CF}$ and in the same way you can see C5. C5 is further coupling is very small because it is 1, 2, 3, 4 bond coupling. So, you can see here $^{4}J_{CF}$ and then 4, 4 will be little here 1, 2, 3. So, 3 bond coupling will be there and 3 will be ^{2}J coupling and then 6 does not show any coupling as it is very far. That means if we have another NMR active nucleus the assignment becomes much more simplified just by looking into the magnitude and how farther this nucleus is from the nuclei under consideration. We should be able to elucidate the structure very easily, this is how one can use other NMR active nuclei present in a molecule for better interpretation. Now, let us look into symmetrically substituted compound. Here we have at 1 3 positions substitution is there.

So, now, these two are identical and these two are identical and this is different and this is different. That means one can anticipate one four signals for this difluorobenzene, meta difluorobenzene you can see here we have 1 2 3 4 5, 5 are there and 4 and 6 appear together the reason is although we say these two are chemically equivalent, their interaction with fluorine is very different. For example, this one has a 2 bond coupling with fluorine they are identical, we have C2 axis of rotation, but still 6 interaction with fluorine F1 is different from F2 and similarly interaction of 4 with F1 is different from F2 as a result we get a different pattern here, whereas C2 shows very nicely a triplet and then C5 will also show a triplet here. And then C1 shows a doublet and C3 will also a doublet of almost same

coupling value, whereas here this portion, we have a different spin system. It appears something like this here. So, this we call it as virtual coupling. Now, let us try to analyze ^{1}H NMR data for better understanding. Again, the presence of a paramagnetic center with one or more unpaired electrons in a compound has significant influence on ^{1}H NMR spectrum chemical shifts.

First the local magnetic field at each of the ^{1}H nucleus is affected when NMR active nucleus is placed in an external magnetic field. The energy difference between nucleus spin states arises due to the interaction of the magnetic fields of the spinning nuclei with the applied field. However, the local field experienced by the nuclei is not the same as the applied field because the electron pairs in the vicinity of the hydrogen nucleus generate small local magnetic fields and these magnetic fields as I had mentioned earlier, can align with the magnetic field or they can oppose the magnetic field depending upon their alignment. We will see some sort of shifts and also the further splitting. The local magnetic field is the sum of the applied field and all the smaller fields, the later depend on the chemical environment of the hydrogen nucleus. This is very important. So, all these chemical shifts essentially depend on chemical environment of the hydrogen nucleus. Typically, the difference in local magnetic fields for protons in the different environments are small and as a consequence the chemical shift range over which the ^{1}H NMR is not large.

So, whatever the chemical shift difference that we come across that is considerably low compared to other nuclei as a result we have a small spectral range of 1 to 10 ppm in case of ^{1}H NMR. In a paramagnetic compound there is an additional factor, a large local magnetic field is arising from the unpaired electrons or electrons on the paramagnetic center. So, when we have paramagnetic center, what happens, because it generates again another magnetic field that can again oppose or align with the magnetic field, and hence we see unusual shifts in such molecules and this happens especially in case of metal complexes, where we have lot of unpaired electrons and if it is diamagnetic it is not an issue. If the complex is paramagnetic, due to unpaired electrons and if we have some

hydrogen atoms attached directly to metal, will be shifted to towards shielded region. This contributes to the energy difference between the nuclear spin states and as a consequence the chemical shift range for the ^{1}H NMR signals is much larger than in a diamagnetic component, which can go up to -15 to -20, or it can go up to even -60 sometime. The second effect that is observed in ^{1}H NMR spectra of paramagnetic compounds is broadening of the signals.

This effect has its origins in a significant shortening of the excited state lifetime. The relaxation time is very short, that means we have to look into relaxation time: we have spin-spin the relaxation spin lattice relaxation, what would happen to this relaxation, if we have paramagnetic species. Anyways, since I am more focusing on interpretation, I am not going to the details of those things. If you want to look into the details of those aspects, I am sure there are better courses, where theoretical aspects are discussed in detail. Probably; you can refer to those or you can read appropriate book for that one. So, in some cases the broadening is so great that no well-resolved signals are observed. In some cases, probably we may miserably fail to record a spectrum because of paramagnetic species present in a molecule. So, let us consider a simple paramagnetic species, tris-phenanthroline Cobalt [Co(II)]complex. Here Co(II)can have one or three unpaired electrons in an octahedral environment depending upon the ligand field strength. So, if you see this is d^7 system. We can have something like this or we can also have something like this, if it is low field or low spin. So, we can have either one or three unpaired electrons. It is very interesting to examine the ^{1}H NMR spectrum of this complex tris-phenanthroline. There are four different automatic proton environments in this one and the chemical shifts of the signals assigned to these ^{1}H nuclei fall in the range of +110 to +15. So, you can see otherwise, most of the organic molecules, the chemical shifts are confined to 1 to 10 ppm, whereas in this case it can go to as low as +110 to +15 or in some cases it can also go to -15 or -20. Let us see here, what are those four signals we are getting due to which protons? you can see here. I have labeled one phenanthroline molecule, here others are also identical, so you can label them as 1 2 3 and then 4 here and similarly 1 2 3 and 4 here. So, four signals we are seeing in this +110 to +15 range I would come back again to ^{13}C and ^{1}H wherever we come across spectrum or at the end I will be discussing problems where I would take NMR

spectra along with IR and UV data to elucidate the structure. So now let's focus our attention to phosphorus ^{31}P NMR. ^{31}P NMR is very similar to ^{1}H NMR, the concept of ^{31}P NMR is very similar to proton NMR. Here also we have natural abundance of ^{31}P 100 percent, and nuclear spin I equal to half (I = ½).^{31}P nucleus is a useful NMR spectroscopy tool due to its relatively high gyromagnetic ratio of 17.235 megahertz per Tesla for ^{1}H if you recall it is 42.576 megahertz per Tesla and in case of ^{13}C it is one-fourth of ^{1}H so it is around 10.705 megahertz per Tesla. The spectral interpretation is much easier and also it is very similar to ^{1}H NMR. ^{31}P NMR is an excellent technique for studying phosphorus containing compounds such as organic compounds, coordination complexes and molecules of biological importance and also in materials, where we have phosphorus and also, especially very useful in understanding the intermediates in homogeneous catalysis, if you have phosphorus ligands in those metal mediated catalytic reactions and now let us try to look into the differences between ^{1}H and ^{31}P NMR. ^{1}H NMR spectra is referenced to TMS, tetramethylsilane, whereas in case of ^{31}P NMR, we are using 85 percent phosphoric acid (H_3SO_4) and we are considering its chemical shift as 0 and it is used as an external standard because we cannot add 85 percent H_3SO_4 directly to the solution containing phosphorus compounds as it can react with it. It is used as an external standard. Another standard is trimethyl phosphate or trimethoxyphosphine also used as a standard and unlike phosphoric acid it is independent of concentration or pH so we can use it without any problem and with respect to phosphoric acid the shift of trimethyl phosphate is around 140 ppm. Similar to ^{1}H NMR, positive chemical shifts correspond to downfield shift from the standard chemical shifts. ^{31}P NMR commonly depend on the concentration of the sample the solvent used and the presence of other compounds this is because the external standard does not consider the bulk properties of the sample. As a result, the reported chemical shifts for the same compound could vary by 1 ppm or more especially for phosphate groups whenever we have a pentavalent phosphorus having P double bond O (P=O). In this case, what happens the chemical shifts for the same sample if you record and there can be some variation it's because of homogeneity problem and other things as I mentioned here since the bulk properties are not considered here so that can show this kind of variation ^{31}P NMR spectra are often recorded with all proton signals decoupled very similar to decoupling process we use in case of ^{13}C here also conveniently we can use decoupling process and

we can record ^{1}H decoupled ^{13}P NMR $^{13}P\{^{1}H\}$. that will be very simple and it's very simple to assign. This gives rise to single sharp signal per unique phosphorus and here in we consider both coupled and decoupled spectra but very nicely we can see two phosphorus coupling up to three, four or five bonds they are chemically and magnetically non-equivalent interpretation of spectra easy very similar to ^{1}H as I mentioned earlier as in ^{1}H NMR, phosphorus signals occur at different frequencies depending on the electron environment of each phosphorus nucleus. So, let us consider some examples here. You can see the extensive list of chemical shifts and the chemical shift range for various type of phosphorus compounds we come across.

So, let me elaborate on this one in my next lecture until then have an excellent time reading on spectroscopy thank you.