Interpretative Spectroscopy

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Lecture 18

^{19}F , ^{14}N and 15N NMR Spectroscopy

Hello everyone, it is a pleasure to welcome you all once again to MSB lecture series on interpretative spectroscopy. In my last lecture, I showed you how nicely we can use phosphorus NMR to monitor a reaction and also, we can gauge when the reaction is going to end and also whether product formed or no other than the expected product. So, now let us continue looking into more such examples, of course using several other NMR active nuclei as well. Now, let us look into the ^{19}F NMR and of course about the abundance gyromagnetic ratio all those things I have given in the beginning. Now let us focus our attention to the chemical shift values as far as ^{19}F NMR is concerned. ^{19}F is 100 percent abundant and I equal to half (I = ½). Again, it is as simple as ^{1}H or ^{31}P to measure and understand.

So, here if you just look into CF here, we have something like this on an alkane chain. Reference, we are using is $CFCl_3$. So, relative to trifluoroacetic acid, it will show around -131 or with respect to mono fluoro benzene, it comes around -96, but with respect to $CFCl_3$ it comes at -210. Different references are used, that is the reason I have given the value relative to different standards. And then in case of two fluoro groups present on same carbon, we see a peak at -140 in case of $CFCl_3$ and -69 with trifluoroacetic acid and -26 here. In fluoro aromatic compounds, the range is -140 or -60 or- 26. And then in case of fluorine atoms present next to carbonyl group, the ranges are -125 or -46 or -11 and again we have a CF_3 group next to a CH- 75, 4 or 39 and then a CF_3 group next to carbonyl group would appear at - 81 or -2 or 33 and if you have a sulfonate group it comes at -50 or 129 or 164. These are some of the important ones besides that we have numerous compounds.

For example, if somebody asks you to sketch the ^{19}F NMR spectrum of ClF_3. Simply by looking into valence shell electron per repulsion theory, you should be able to arrive at the right kind of geometry. For ClF_3 and then again let us recall your basic understanding of VSEPR theory.

So, valence shell electron per repulsion theory, the abbreviation is self-explanatory and now if you just look into the valence electrons present on chlorine and fluorine atoms, we are talking about 7 plus 3 here. So, 10 electrons are there 10 electrons means steric number equal to 5. 3 bonded pairs are there and 2 lone pairs are there. So, the preferred geometry for steric number 5 is trigonal bipyramidal and when you have trigonal bipyramidal with 3 bonded pairs and 2 lone pairs, all these possibilities are there and then we have to look into lone pair : lone pair, lone pair : bond pair and bond pair : bond pair repulsion, and from this basic knowledge we will arrive at the right structure where we have 2 lone pairs in the plane and then 1 fluorine atom also in the equatorial plane and other 2 fluorine atoms being axial. So, this is the right structure and also, we say that it has a T shape and then we have to sketch the ^{19}F NMR spectrum of this one here, assuming this molecule is static. We can anticipate 2 types of fluorine signals: one is due to axial one the other one is due to equatorial. Equatorial one will be coupled with 2 axial ones to give a triplet and then 2 axial fluorine atoms will be coupled with equatorial one to give a doublet; the spectrum should show a doublet and a triplet something like this.

So, this is how the ^{19}F NMR spectrum of ClF_3 looks like. Now let us look into another interesting molecule. Again, some of these molecules are really meant for explaining VSEPR theory. SF_4 very interesting to look into the shapes of the molecules or species and also the geometry, and you should remember the difference between the shape of a molecule and geometry of a molecule. When we define the geometry of a molecule, like this, we have to consider both lone pairs and bonded pairs, that means the entire steric number has to be considered while defining the geometry, but while defining the shape we can ignore the lone pairs; that one should remember. Sketch the ^{19}F NMR spectrum of SF_4, of course SF_4 also same thing, if you look into SF_4 we have 6 electrons are here and sulfur s^2p^4 and we have 4 electrons coming. So, we have 10 electrons are there and steric number is 5 and here 4 bonded pairs are there and 1 lone pair is there. So, that means again trigonal bipyramidal geometry with trigonal bipyramidal geometry what basically happens is one something like this if S is here what we have is 1 fluorine here 1 fluorine here and lone pair is there. So, lone pair is occupying trigonal planar position and then this is a trigonal bipyramidal molecule, but the shape is seesaw and also to minimize these repulsions what happens they are further bent little bit in this fashion.

That means here just by simply looking into the molecule we can say that there are two types of fluorine environments and two axial ones and two equatorial ones. So, when we look into the signals we anticipate two type of signals and each signal will be a triplet. So, that means we can see two triplets for SF_4 here. So, it should something like this.

So, one for axial, one for equatorial, and then this is the FF coupling, the spacing what we see here; it is FF coupling. So, this is how we can sketch the ^{19}F NMR spectrum of SF_4. Let us look into another molecule here. Now, we have taken SeF_4 you know that the ^{77}Se is NMR active with I equal to half ($I = \frac{1}{2}$) and it is only about 7.6 percent; rest ^{78}Se is NMR inactive.

So, when we look into ^{19}F NMR, we can see again very similar to SF_4, it has a see-saw type structure. So, with color, we can distinguish them. If you look into ^{19}F NMR again, we are seeing a triplet in each case triplet. Again because of selenium being NMR active, that is present is in 7.6 percent or so what happens we can see satellite peaks. That means basically if you see a triplet something like this. So, let me make it little bigger, now we can see this coupling will also have this. $^{1}J_{FSe}$ coupling and then what you see here is this spacing is $^{2}J_{FF}$ coupling.

So, same thing happens in both the cases both, we get a triplet of a triplet and also a triplet of doublets that would be here. So, this happens in both the cases, but when we look into 77th selenium NMR what basically happens is you get a triplet first this is coupled with axial ones and then each one will be split further into triplet into equatorial ones. So, if I applied this one it should be 1 :2 : 1. So, this how we can sketch both ^{19}F NMR spectrum as well as 77 NMR spectrum for SeF_4. So, you can see here triplet of triplet it is pretty easy right.

So, now let us look into another example here the SiF_4. SiF_4 is a tetrahedral molecule and if you look into fluorine NMR this is fluorine NMR fluorine NMR would not show much difference because all fluorine are in single environment here, but you should remember the fact that silicon has 3 isotopes ^{28}Si, ^{29}Si and ^{30}Si. Silicon and then ^{28}Si is 92.23 percent ^{29}Si is 4.67 and this is 3.10

^{28}Si and now this is I equal to 0 ($I = 0$), this I equal to half ($I = \frac{1}{2}$) and then again this I equals

0 (I = 0). So, that means basically we should think of a signal coming here without involving any coupling in case of ^{19}F this corresponds to 92 means 95.33 which is NMR in active I equal to 0 (I = 0) and this one is $^1J29_{SiF}$ coupling that is about 178 hertz and if you look into intensity this correspond to 2.32 or 2.32 or something like that.

So, this is how satellite peaks appear, but if you look into ^{29}Si NMR. It looks all fluorine atoms being identical. All 4 fluorine atoms would split silicon signal into a quintet. we do not use the term pentet for 5; we use the term quintet. So, we have 1 : 4 : 6 : 4 : 1, we are getting something like this and here again if you look into the coupling the magnitude of this one should be the same as this one. So, double verification we can do. So, silicon NMR looks like this; ^{29}Si NMR for SiF_4 would be a quintet you see now how simple. Let is to look into various other NMR active nuclei other than ^1H and ^{13}C and also ^{31}P.

Let us focus our attention to two more NMR active nuclei that is nitrogen ^{14}N and ^{15}N. The ^{14}N NMR experiment is much less sensitive than ^1H, but has a larger chemical shift range and signals are broadened due to quadrupolar interaction of ^{14}N having I equal to 1 (I = 1). So, larger the molecule, and symmetric the nitrogen environment and broader the signal. This one should remember. If running ^{14}N or ^{15}N is inevitable; ^{15}N there should not be any problem, but if you are running ^{14}N, what we should remember is the larger the molecule and the more symmetric the nitrogen environment, broader the signal. The small and highly symmetric aqueous ammonium ion gives a very sharp line less than ^1H wide. The larger and less symmetric the molecule, the wider the signal. Smaller and more symmetric the molecule, the sharper the signal. Symmetric aqueous ammonium ion gives a sharp line with less than ^1H width. So, on the other hand, if you look into liquid ammonia being less symmetric, the width is 16Hz on a 400 MHz spectrometer at room temperature and urea is larger and asymmetric. So, the line width is approximately 1 kilohertz you see very broad signal.

So, molecules that are significantly larger than urea yield signals too broad to be observed with a higher resolution NMR spectrometer even with a 600 MHz, it is very difficult to observe. Since the nitrogen chemical shift range is wide, may be readily used for distinguishing nitrogen species in very small molecules and if you want to run ^{15}N it has to be preferably enriched otherwise the percentage is so low it is very difficult to know, how much percentage is there. So, for example natural abundance of ^{14}N is 99.63 and chemical shift

range is 900 ppm; from 0 to 900 ppm and frequency ratio is also given for ammonia and reference compound is nitromethane in $CDCl_3$ and line width of reference is 19 Hz and T1 relaxation time is also given and when all this vital information is given, and one should keep these things in mind especially when you want to run ^{14}N. Of course, ^{15}N is very very important from biological point of view because we have lot of compounds. Now, as I mentioned if the molecule is more asymmetric the line width will be more; you can see here, the spectrum of urea; it is very huge and then if you see here NH_3 in liquid very small and less symmetric.

So, 16 Hz is there, if you see NH_4^+ very small and highly symmetric you can see the line width is 0.8 it looks like ^{13}C NMR or phosphorus NMR very simple. So, that means if you have smaller molecules and are symmetric looking into ^{14}N NMR would be rather easy. So, this plot is essentially to show how the line width varies with the molecular symmetry and also the size. Now, this is ^1H NMR spectrum of ammonium chloride this is a tetrahedral molecule you can see NH_4^+ plus and then these 4 protons are identical and they are coupled with nitrogen, nitrogen, I equal to 1 (I = 1).

So, you see a triplet of equal intensity 1 is to 1 is to 1 here and then the $^1J^{14}_{NH}$ coupling is 52.4 Hz. So, what is interesting is, in this one we are also seeing very tiny peaks here. This is due to ^{15}N which is less than 0.4 percent and $^1J^{15}_{NH}$ coupling is 73.5 Hz, probably they have taken much longer time to identify these two peaks here. These are the ^{15}N satellites. This was observed in case of ammonium chloride.

You know that ^{14}N coupling constant is smaller compared to ^{15}N coupling because ^{15}N has lower resonance frequency. Now, if we look into ^{14}N NMR spectrum of ammonium chloride, ^{14}N is equally coupled to four equivalent hydrogen atoms, as a result it shows a quintet of this type. So, ^{14}N NMR spectrum of ammonium chloride consists of quintet, whereas ^1H NMR spectrum of ammonium chloride consists of triplet of equal intensity; 1 : 1 : 1 line and of course, this also you can say, it is a EX_4 spin system. Look into this molecule here, ^{15}N enriched cyclosporine-A in $CDCl_3$ this spectrum was acquired in 1 hour. Very interesting, beautiful spectrum for this ^{15}N because it is a ^{15}N enriched molecule here. Still it took 1 hour for acquiring the entire data to identify all these: 1 to 11 nitrogen atoms. To obtain similar sensitivity without enriching would take about 10 years of scanning. That means, basically

we have to take this sample, put into NMR spectrometer may be 600 megahertz run continuously ^{15}N NMR for 10 years without stopping to see something like this. So, you can imagine the presence of ^{15}N so low and then how much sample is needed and how much time it takes, but on the other hand when you enrich with ^{15}N it appears like any other simple molecules and measuring ^1H NMR spectrum. You can see all ^{15}N are here 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11.

In biological studies, ^{15}N plays a major role. So now this one is for sodium azide. Sodium azide has two different types of nitrogen atoms: one is cationic and other two are anionic and sodium plus. So, it is neutral and then the middle one is appearing here and these two anionic are appearing here and the ratio is 1 : 2. So, this is ^{15}N V enriched sodium azide taken in D_2O. So, let me show you another very interesting example. This is about ^{13}C NMR, the structure of tertiary butyl lithium is very similar to that of methyl lithium. We know that methyl lithium has a cubane structure, where alternate corners are occupied by methyl group and lithium with four lithium atoms having tetrahedral relationship, but with each hydrogen atom replaced by a methyl group, you get tertiary butyl lithium, and that also has very similar structure to that of methyl lithium cubane structure. The 75-megahertz ^{13}C NMR spectrum of a sample of tert-butyl lithium prepared from ^6Li metal consists of two signals: one for the methyl carbons and one for the quaternary carbon atoms. That means if you look into ^{13}C NMR spectrum, we get two signal sets, one is for quaternary carbon directly interacting with lithium, the other one is methyl groups. So, now if you focus your attention to the quaternary carbon, the spectrum looks like what I have shown here at 185K, that is, at low temperature, it shows seven lines, a typical septet. On the other hand at 299K, that is, at room temperature it shows nine lines.

So, now we have to analyze and explain, why at low temperature, ^{13}C NMR spectrum for quaternary carbon shows a septet, whereas at room temperature or 299K, it shows a multiplet having nine lines. Now let us look into the cubane structure. This is how you can show the relationship of four lithium atoms in methyl lithium or tertbutyl lithium. This is tetrameric and then in each face, we have carbon is sitting like this. It is methyl or tertbutyl group and that means at 185K, what happens? this molecule is very static. When it is static, the carbon present in one of the triangular phases would see only three lithium atoms,

because the whole molecule has no fluxionality, and it is very static and it is sitting something like this overlapping with 2s orbitals of four three lithium atoms and it is a four centered two electron bond system. So, in this case, it identifies all equally. That means the carbon is split by three equivalent lithium atoms. If we use 2nI + 1 rule, at low temperature we have three and I equal to +1. It shows seven lines (2*3*1+1 = 7). So, this is carbon in one but when you look into room temperature it is no longer static. So, all lithium atoms are exchanging. As a result, carbon sees four equivalent lithium atoms and they will be exchanging.

 Now, four equivalent lithium atoms are there at 299K. So, what would happen is if you use again 2nI +1 rule, we have four identical one (I=1). So, we see nine lines here (2*4*1+1 = 9). This how even the dynamic process can be understood readily using NMR spectroscopy.

 So, let me continue in my next lecture more details and more examples. Thank you.