Interpretative Spectroscopy

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Lecture 04
Introduction to the concept of Chemical Shifts in NMR spectra

Hello everyone, once again I welcome you all to MSB lecture series on interpretative spectroscopy. This is the fourth lecture in the series, in my previous lecture I started discussion on chemical shifts, the NMR signals we call it as chemical shifts. Let us go back to those few points in NMR spectrum. We get NMR signals, what these signals say about the molecule. So, that means, the number of signals show how many different kinds of protons are present and then the location of the signals shows how shielded or deshielded, this is very very important information and then the intensity of the signals show the number of protons of that type. So, one is different type of signals and where they are appearing and then how many protons are there in each signal and then the signal splitting, what is the splitting pattern; whether two lines are there, three lines are there or four lines are there, one line is there. So, this signal splitting shows the number of protons and adjacent atoms that means how they are connected.

As I mentioned in case of ethanol we have CH_3, CH_2, OH when all these points will tell you where CH_3 is located, where CH_2 is located, where OH is located and then how many different type of hydrogen atoms are there and each one how many are there hydrogen atoms and where they are appearing and then the splitting would tell you whether CH_3 is close to this one something like this. So, all this information again comes very nicely without compromising whatever the information we get from the bonding concept; valence bond theory or molecular orbit theory. In the same way, it proves the presence of these signals, these groups at appropriate place. So, this is where the importance of NMR comes in characterizing molecules. We call these signals as chemical shifts, they are measured in parts per million. The ratio of shift down from TMS to total spectrometer

frequency in hertz (Hz) will give you parts per million in ppm. Chemical shifts in parts per million is independent of magnetic field strength that means whether you measure chemical shifts at 60 megahertz (MHz), 100 megahertz (MHz), 300 megahertz (MHz) or 500 megahertz (MHz) or even in 1000 megahertz (MHz) the value remains same as far as these chemical shifts are in parts per million (ppm).

So then we use the scale called delta scale (δ). When we measure it in parts per million (ppm), we use delta scale and then just make you familiar with chemical shift terms. I am going back again to the basics what I discussed in my first lecture. So, this one is induced magnetic field opposite to the applied magnetic field; if you just see here m equals plus half ($m = + 1/2$) orientation of nucleus, orientation of nucleus is like this and then the precision of electron density surrounding this proton and induced magnetic field, due to the circulation of electron density opposing here, opposing the applied magnetic field. So that means applied magnetic field will cause the electron to precess about B naught (B_o) which in turn causes the circulation of electron density and generation of a small magnetic field B_i. You can see here, this is B_i, green one I have shown. So as per Lenz's law, the direction of an induced current is such as to oppose the cause and hence direction of B_i is always opposed to the applied magnetic field.

Now the net magnetic field experienced by the nucleus is B_{net} equals B_o - B_i ($B_{net} = B_o - B_i$), so the magnetic field experienced by the nucleus is less than the applied magnetic field and hence a lower frequency. Now in order to cause transition you have to apply a less frequency in a direction perpendicular to applied magnetic field. That means the electron density surrounding the nucleus produces a shift to lower frequency. So, as a result, what happens you can compensate whatever the loss by reinforcing this one so that you can keep the Larmor frequency constant or you have to bring down the magnetic field strength of the B_i, by applying a field orthogonal to B_o that should correspond to now the precision frequency. So, this is where the terms low frequency, high frequency, low field shift or high field shift; all those things come into picture.

So that means this can also be represented by B_{net}, net magnetic field experienced by the nucleus ($B_{net} = B_o (1 - \sigma)$), here σ is referred to as the shielding constant. So, if you keep the Larmor frequency constant we need to increase the magnitude of B_o to achieve

resonance. As I said, equivalent to B_i you have to apply a field so that B_o is strengthened now to neutralize the effect of this one. That is the reason it is called up field or higher field strength or also called diamagnetic shift. Why we are using term diamagnetic later we will be coming with another term called paramagnetic.

So diamagnetic shielding and paramagnetic deshielding will come. So as a result of diamagnetic shift, all signals will be shifted to lower frequency. Deshielding is referred to as down field, lower field or paramagnetic shift; all shift to higher frequency where the induced magnetic field will be reinforcing the applied magnetic field. In that case what happens net magnetic field experienced by the nucleus will be much more than the magnitude of B_o. This is called paramagnetic shift or paramagnetic deshielding.

So the extent of magnetic shift is determined by the amount of electron density surrounding the nucleus. These points are very important; these three points I have shown here. The extent of diamagnetic shift is determined by the amount of electron surrounding the nucleus, the ease with which electron density can circulate about B-naught (B_o), and the magnitude of B-naught (B_o). That means the amount of electron surrounding the nucleus and also the ease with which electron density can circulate about Bnaught (B_o). That means how many electrons are there in the valence shell, whether they are spherically symmetrical or unsymmetrical field and also the magnitude of Bnaught (B_o).

At constant B-naught (B_o), the shift is dependent only on the amount of electron density and the symmetry of the electron density. It is not only the magnitude of the electron density, the symmetry of the electron density is also very important in generating opposite field or aligned with the field in generating diamagnetic shielding or paramagnetic deshielding. Let us consider ^{13}C nucleus. Here I = ½. Here nucleus is surrounded by $1s^2$ $2s^2$ and $2p^2$ electrons in the valence shell; so, 6 electrons are there. That means here compared to ^1H, the electron density is more and hence the magnitude of induced magnetic field, B_i will also be greater.

So if you compare the nucleus of hydrogen kept in a magnetic field and ^{13}C nucleus kept in a magnetic field, if both are generating induced magnetic field, the magnitude of the induced magnetic field generated by carbon is much more than that of hydrogen because there electron density is only $1s^1$, whereas, here we have $2s^2\ 2p^2$. So, the electron surrounding the hydrogen nucleus is spherically symmetric, whereas, in case of ^{13}C electron density is due to $1s^2\ 2s^2$ symmetric, but the same due to $2p^2$ is not spherically symmetrical. So this is important, that means in case of ^{1}H still we have 1 electron and the 1s orbital is l, spherically symmetrical, in case of ^{13}C electron density due to $1s^2$ and $2s^2$ are spherically symmetric, whereas, that of $2p^2$ is not spherically symmetrical. So only way to obtain spherically symmetrical is by having $1s^2\ 2s^2$ and $2p^6$ so that the electron density is equal in all the three directions. Orbitals px, py and pz are orthogonal to each other if all of them are completely filled, then you can have electron density equal in all the directions x, y and z. As a result, probably, there will be spherically symmetrical distribution of electrons. If we are talking about C4 minus (C^{4-}) ion, if not with electronic configuration of $1s^2\ 2s^2\ 2p^6\ 2p^2$, it is not spherically symmetrical and it is very different from that of ^{1}H generated induced magnetic field. Here it is, there so I can write here this is called whatever the reference is there right side whatever it comes low frequency shift up field shift and then higher field high field and shielded shielding. So, here high frequency because in this case what happens it is reinforcing so it is high frequency shift and this is low/down field shift and high field is low field shift and then shielding and deshielding.

So, this is how we designate with respect to reference here. That means the lack of spherically symmetrical electron density surrounding the ^{13}C nucleus results in diminished circulation of electron density and hence lower B_i. If the spherical symmetry is not there for the induced magnetic field, a small value for B_i and as a result the shielding effect is minimum. I repeat it again; the lack of spherical symmetry for the electron density surrounding the ^{13}C nucleus, results in diminished circulation of electron density and hence lower the B_i value. So, the shielding constant sigma can be divided into: considering the nature of the electron density, whether it is spherically symmetrical

or unsymmetrical; the two components: sigma-d (σ_d), diamagnetic shielding and sigma-p (σ_p), paramagnetic deshielding. So, this one can be divided into two, that means basically it is a combination of sigma-d (σ_d) and sigma-p (σ_p), whereas sigma d is diamagnetic shielding and sigma-p (σ_p) is paramagnetic deshielding. Sigma d results from the unhindered circulation of electron density which produces B_i opposing B_o and hence is always positive and results in shielding. So, that means sigma d results from the unhindered circulation of electron density. Unhindered circulation of electron density happens when it is spherically symmetrical, which produces B_i and that always opposes B_o and it always positive then the net effect is shielding. Sigma-p (σ_p) results from the hindered circulation of electron density, when the electron density is unsymmetrical, then that results in hindered circulation of electron density, which produces B_i aligned with B_o or reinforces B_o.

So, in this case, if this is B will be like this B_i, whereas in this case this is applied. So, in this case this will also be like B_i. So, B_{net} is $B_o + B_i$. So, this is always negative. So, that means the shielding constant is the sum of sigma-d (σ_d). Total effect of sigma-d (σ_d) and sigma-p (σ_p) at a given time whichever is dominating would decide whether the signal is shielded or deshielded.

So, now let us consider two examples of H_2 and F_2, ideal examples to look into these aspects sigma-d (σ_d) and sigma-p (σ_p) components and total screening constant or shielding constant. So, now, if you just take the atomic species in applied magnetic field you can have all possible orientations of this diatomic species, but you can consider the average of all possible orientations that falls into two categories. One is perpendicular to the applied magnetic field, one is parallel to the applied magnetic field. So, that I have shown here. So, this one A diatomic molecule with orientation in perpendicular fashion, here and then in this one parallel here, with respect to the applied magnetic field. So, here cylindrical symmetry related to B_o is there.

So, that means the electron density around atom A is affected due to its bonding with another A. That means earlier when we had simple A that is a different environment.

Now, we have A-A bond and A-A bond has two electrons. Now, the electron density around atom A is affected due to its bonding with another A. Even hydrogen atom in H_2 no longer has spherical symmetry because of the distortion of the electron density by the other nucleus, but in the parallel orientation of H_2, in this magnetic field, the electron density has cylindrical symmetry in the direction of B_o. So, this is not unimpeded and the paramagnetic component is 0.

So, here paramagnetic component is 0, in this case, but in the perpendicular orientation the electron density around each hydrogen is not symmetrical with respect to B_o. However, so sigma-p is negative (σ_p). So, since hydrogen is only surrounded by 1s electron and s orbitals are spherically symmetrical, as a result what happens, still the electron density is spherically symmetrical, as a result the magnitude of sigma-p (σ_p) component that generates because of hindered electron circulation is negligible and B_i only 15 percent. So, sigma-p (σ_p) term for H_2 is negligible.

That means, it is only sigma-d, diamagnetic shielding is what matters in case of H_2 molecule. Now, let us look into F_2. here for the F_2 molecule, the analysis of parallel orientation and perpendicular orientations are very similar to that of H_2. Each F atom has a close shell of electron density. If you take F. So, something like this we have F-F. So, in the perpendicular orientation due to the presence of p electrons and the incumbents of the circulation of electron density about B_o, due to the F-F bond, produces paramagnetic deshielding.

So, in this one electron density is more and we are talking about p-orbital. As a result, circulation of electron density, there is an encumbrance of circulation of electron density hindrance is there as a result produces a considerable amount of paramagnetic deshielding. That means, sigma-p (σ_p) term is quite large. So, actual shielding observed is average of the shielding in all possible orientation. if you ask me a question, why I am considering only perpendicular, why not parallel and perpendicular? Yes, these two are taken after considering averages shielding in all possible orientations. When you consider all possible orientations in all angles you have to take two extremes: one is perpendicular,

one is parallel. Only the average of those two is considered. So, because of this reason except for ^{1}H and alkali and alkaline earth metals where we come across only s electrons in the valence shell, paramagnetic term dominates and hence deshielding is there. We should remember, if we consider ^{1}H NMR, sodium NMR or any other alkali earth metal NMR, lithium NMR, in all these cases what happens paramagnetic term is not there and shielding s there, but apart from this one, if you take any other element, where we have p orbitals with valence electrons, the paramagnetic term dominates.

So, fluoride ions show a chemical shift of 400 ppm compared to bare fluorine nucleus whereas in case of F_2 the paramagnetic deshielding increases its chemical shift to 600 ppm relative to fluoride ion. So, you can see, a remarkable contribution comes from sigma-p (σ_p) term because of hindered circulation of electron density as a result of p electrons. So, this will give you some idea about paramagnetic deshielding and diamagnetic shielding and also why we have in case of ^{1}H alkaline and alkaline earth metals a short chemical shift range, whereas in case of other nuclei, we have a long range of chemical shifts. This is the delta scale chemical shift in ppm. I am telling again shift down from TMS in case of ^{1}H and ^{13}C spectrometer frequency in megahertz (MHz). So, here as I said if you measure chemical shifts in ppm this is independent of magnetic field strength.

So, to compare that one, you can see here: I have taken 60 megahertz (MHz) and 300 megahertz (MHz) and then if you take the chemical shift here 1, 2, 3, 4, 5, whatever you have taken it does not change. It does not change, it remains in ppm steady whereas, in hertz (Hz) it is changing but in ppm it does not change. So, this is the advantage and for the same reason always chemical shifts are given in parts per million (ppm). So, that when you take NMR spectrum in different magnetic field strength, it should not really matter. So, now let us look into the location of signals.

So, after understanding what is chemical shift and what is shielding what is deshielding, let us look into the location of the signals and location of the signal is given by chemical shift. As I mentioned, if you just look into NMR signal, chemical shift of methane, it comes around 0.2 delta (δ) or 0.2 ppm and then if you look into methyl chloride it comes

around 3 and then if you just compare between CH_4 and CH_3Cl, this delta coordination shift ($\Delta\delta$), the change in the coordination shift is 2.8 and then if you add one more chlorine, dichloromethane it is 5.3 and the difference is 2.5. If you take chloroform, $CHCl_3$ it is 7.2 and again difference is 1.3. That means, addition of each chlorine atom changes the delta of remaining protons by 2 to 3 ppm. So, that means, it is additive, here you can see here every time, we are replacing one hydrogen by chlorine the difference is increasing by about 2 to 3 ppm.

That means, it indicates nearly additive. So, you should be able to check whether this holds good in case of all or this is an exception, you can examine yourself. So, that means, more electronegative atoms deshield more and give larger shift values. So, that means, here we have 3 chlorine atoms and more deshielding is there because the electron density is pulled towards them and as a result chemical shift is larger. Then effect decreases with distance.

So, here these chlorine atoms are 2 bonds apart yes if I write like this, 2 bond apart 1 and 2 bond apart. So, effect decrease as the distance between these will move. So, effect decreases as the electronegative atoms are moving farther from the nucleus we are considering. So, additional electronegative atoms cause increase in chemical shift. If I keep on adding more and more electronegative atoms, the chemical shift value will increase.

So, I have given chemical shift values for different type of protons here. You can see here, methyl groups in alkane comes around 0.9 and in alkane again if you look into CH_2 groups it comes around 1.3 and CH will be coming at 1.4 and then if you have a CH_3 group next to a carbonyl group it comes around 2.1 and if it is next to acetylene, it comes around 2.5.

Next what happens if CH_2 is next to halogen or oxygen it will be in the range of 3 to 4 and next in the olefin sudden jump is there it is 5 to 6 and then when we have a methyl

group in a olefin it is again 1.7 and then if you consider OH group in phenol, phenol it is there. So, it comes around 7.2 and then in this one CH will be red one, I have shown here 2.3 and then in aldehyde it comes around 9 to 10 in acid it comes around 10 to 12 in alcohols it comes around 2 to 5 and then in aromatic alcohols it comes around 4 to 7 and of course, here this is incorrect.

So, this is for the aromatic hydrogen atoms. It comes around 7.2, whereas here for aromatic alcohol (phenols), H will come around 4 to 7, amines it comes around 1.5 to 4, and sometime it can also go much lower. I have given some nuclei again and also, I have shown their natural abundance, the nuclear spin values and frequency with respect to hydrogen at 100 megahertz (MHz). I have given also the standard references used while measuring NMR of various nuclei. I have given this important table, you can see ^{1}H 100 megahertz (MHz), the standard we use is tetra methylsilane, we call TMS and same thing is used in case of ^{13}C also TMS, the frequency will be one fourth, 25.1 and natural abundance is 1.1 percent and then ^{19}F, 100 percent natural abundance and frequency is 94, $CFCl_3$ is used as a standard. In case of ^{29}Si again we are using TMS and in case of phosphorus we use 85 percent phosphoric acid. In case of ^{77}Se, dimethyl selenium; in case of ^{103}Rh again 100 percent abundance. The frequency is 3.2 times and rhodium metal itself is a standard there. Then ^{117}Sn natural abundance is 7.7 percent and frequency is 35.6 and tetramethyl tin is used as a standard. We have another one ^{119}Sn this 8.6 percent in this case, we use the same standard and xenon is there $XeOF_4$ is the standard and tungsten we are using Na_2WO_4 and then in case of platinum we are using Na_2PtCl_6 sodium hexachloroplatinate. In case of mercury we are using dimethyl mercury as a reference and corresponding frequency is 16.8 with respect to 100 megahertz (MHz).

Let me stop here and come back with more interesting discussion on NMR spectroscopy. So, have an excellent time reading. Thank you.