

Interpretative Spectroscopy

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Lecture 03

NMR signals and magnetic shielding

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. In my last lecture, I started discussion on nuclear spin and transitions and how energy levels vary with different nuclear spin values. Let me continue from where I had stopped. So, you can see here, with nuclear spin I equals half, we have two energy states here. Plus, half ($+1/2$) state is low in energy and minus half ($-1/2$) is in high in energy. Higher energy ones are represented with downward arrow (\downarrow) indicates, minus half value whereas, upward arrow indicates plus half value (\uparrow). The gap whatever is the distance between them is ΔE equals $h\nu$ ($\Delta E=h\nu$). So, this one can obtain directly from $\gamma B_0/2\pi$ ($\gamma B_0/2\pi$).

So, one can get this information ν directly from $\gamma B_0/2\pi$ ($\gamma B_0/2\pi$). So, where B_0 is the magnetic field strength and γ is gyromagnetic ratio. The magnetic field of the spinning nucleus will align either with the external field or against the field; you can see here. This arrow represents this is aligned with the magnetic field. So, those nuclei which are aligned with the applied magnetic field, they will be lower in energy and those which are against the field are opposing the applied magnetic field, they will be higher in energy they will be having downward arrow.

So, a photon with the right amount of energy can be absorbed and cause the spinning proton to flip, when we know that this gap, if we apply, the right amount of energy that matches this value then, what happens flipping of proton or nucleus takes place. The difference in energy between two spin states over a varying magnetic field, I have shown here. You can see as magnetic field strength increases the gap increases, when the gap

increases energy required will be very high in that case what happens to the chemical shift, that term, I will be introducing later the chemical shift difference between the different nuclei in the same molecule would increase as a result the spectrum will be well resolved and understanding various functional groups present would become very easy. This is the advantage of increasing the field strength. So, now let us look into the energy associated with this nuclear transition and magnet strength as I said the energy difference is proportional to the magnetic field strength, the energy difference between the two nucleus spin states is directly proportional to the magnetic field strength and that is given by this equation $h\nu = \gamma h B_0 / 2\pi$ of course, h h cancels, and it is simplified to become $\nu = \gamma B_0 / 2\pi$. So, gamma is gyromagnetic ratio is a constant for each nucleus and for hydrogen it is 26.753 radians per Tesla per second ($\text{rad T}^{-1} \text{s}^{-1}$) and of course, if you have difficulty in understanding the magnetic field strength in Tesla, one Tesla = 10,000 gauss and gamma gyromagnetic ratio is nothing, but the ratio of its magnetic moment to its angular momentum.

So, in a magnetic field strength of 14,092 Gauss or 2T, a 60 megahertz (MHz) photon is required to flip a proton, that means, you take a proton in a magnetic field strength of 14,092 gauss, the frequency you have to apply, that means, the another magnetic field you are applying in a direction perpendicular to the applied magnetic field should have a frequency of 60 megahertz (MHz) that would cause proton to flip. So, this is low energy radio frequency that essentially whatever the magnetic field we are applying perpendicular to one B_0 or B_i , we call it as, that is a low energy, comes from the radio frequency region. So, what is magnetic shielding? This is very important term when it comes to the utility of NMR in elucidation of the structure of molecules. So, if all protons absorb the same amount of energy in a given magnetic field not much information could be obtained. As I mentioned, if you consider ethanol we have CH_3 group, we have CH_2 group, and also, we have H in OH. If all of them absorb the same amount of energy in a magnetic field then you would observe a broad signal that would not have really helped us in understanding the different groups present in it. So, that means, basically what happens protons in different groups have absorbed different amount of energy for nuclear

transition. Why that happens? protons are surrounded by electrons that shield them from the external field.

So, that means, when we subject a nucleus into magnetic field we are not subjecting a bare nucleus and each nucleus is surrounded by electrons. Depending upon the valence electrons present in that particular atom, these electrons would shield the nucleus from the external magnetic field that is applied. In that case what happens, either the protons would experience more magnetic field or less magnetic field depending upon the nature of the electron density that is circulating about the nucleus. Circulating electrons create an induced magnetic field that opposes the external magnetic field. That means, under the influence of magnetic field the circulating electrons also create another induced magnetic field that always opposes the external magnetic field as a result the net magnetic field experienced by the nucleus will be B_0 minus the induced magnetic field if you say B_i . So, that means, net magnetic field experienced by nucleus is $B_0 - B_i$.

B_i is the induced magnetic field generated by circulating electrons, which always opposes the applied magnetic field, if it is in this direction, this is called magnetic shielding. So, that can be seen here. So, magnetic field strength must be increased for a shielded proton to flip at the same frequency. For example, let us say, we have kept a nucleus at 2 Tesla (T) or 14,092 Gauss and then the electrons would generate a magnetic field that is induced magnetic field that opposes, as a result what happens, the net magnetic field experienced by the nucleus drops. Hence, its precession frequency also drops, in that case what happens. we have to use a different frequency to cause flipping of the nucleus.

That means, here the frequency decreases. That means, either we can decrease the frequency of the applied magnetic field or we can try to balance the applied magnetic field strength to make it what it was before the opposing magnetic field was generated. So, two ways are there. So, electrons shielded the nucleus here and shielded proton feels less than 14,000 Gauss and stronger field need to be applied to compensate for shielding.

That means, either you can enhance this applied magnetic field strength or decreasing the Larmor frequency we used to flip the nucleus.

So, now, the Larmor frequency corresponds to different field strength. I have shown here 14,100 Gauss, it is 60 megahertz (MHz) with respect to proton and in case of 23,500 this is 100 megahertz (MHz) and 47,000 it is 200 megahertz (MHz), 58,700 Gauss it is 250 megahertz and 94,000 Gauss it is 400 megahertz (MHz) and then 117,500 it is 500 megahertz (MHz). So, the different field strength and corresponding magnetic field strength is shown in this slide and also of course, this one little bit more informative. So, here I have given for different isotopes, their natural abundance, the spin and also gyromagnetic ratio and also the corresponding magnetic moment here. If you focus your attention on ^1H it is almost 100 percent abundant 99.9844 the rest is ^2H deuterium and I equals half ($I = \frac{1}{2}$), and the magnetic moment is 2.7927 ($\mu = 2.7927$) and then magneto gyro ratio is 26.753×10^{-7} radians per second (rad s^{-1}). And ^2H very small amount is there and $I = 1$, and its magnetic moment is given and also magneto gyro ratio is also given here. You can compare here magnetic ratio is almost six times less than that of proton and then ^{11}B and ^{10}B , we have as I mentioned ^{11}B we have 81.17 percent natural abundance and spin is $3/2$.

In case of 10 Boron (^{10}B) it is 18.83 and then spin is 3 ($I=3$) and then both of them have different gyromagnetic ratios. That means, this is more sensitive, and this is less sensitive here you can see from this one and ^{13}C , only 1.1 percent ($I=\frac{1}{2}$) is there and the rest is ^{12}C that is NMR inactive ($I=0$). For ^{13}C , magnetic moment is 0.7022 and corresponding magnetogyric ratio is 6.728×10^7 . And then in case of ^{14}N this is 99.63 percent natural abundance, whereas ^{15}N is only 0.37, in most of the natural compounds you do not see neither ^{15}N because of lower abundance nor ^{14}N because of quadrupolar interactions.

In case of ^{17}O hardly, we can come across any oxygen containing molecule exhibiting ^{17}O NMR signals because of very low abundance. In case, if you want to study, we have to enrich those samples with ^{17}O here spin is $5/2$ and then ^{19}F is very important this is 100

percent abundant half spin ($I = 1/2$) and then its sensitivity is pretty good and magnetic gyro ratio is 25.179 the sensitivity wise it is as good as you can see proton here. And ^{29}Si only we have 4.7 percent rest is ^{28}Si . For ^{29}Si , ($I = 1/2$) and then the corresponding magneto gyro ratio is minus 5.319×10^7 radians per Tesla per second. And then other one is very important nucleus as far as the inorganic chemistry is concerned, organometallic chemistry is concerned, and homogeneous catalysis is concerned, this is ^{31}P it is also 100 percent abundant, and I equals to half ($I = 1/2$) and, understanding and interpretation of ^{31}P NMR spectra is as easy as proton NMR. I will be discussing lot of examples of different types of phosphorus containing compounds to make you familiar with interpretation of spectra especially with phosphorus compounds and also in combination with other nuclei where you can come across interaction of phosphorus with either carbon, hydrogen or even with platinum rhodium etcetera. And then here gyromagnetic ratio is 10.840 and of course, the list is quite extensive I have given in the list for most of the elements which are NMR active no matter what their natural abundance is I have given here you can go through this. Those I have mentioned, I have given some Larmor frequencies using these values you should be able to calculate Larmor frequencies for most of the nuclei, we have here which are NMR active.

Try to find out Larmor frequencies at particular field strength and how it compares with hydrogen, that gives some idea about interpretation of NMR spectra and other things such as running NMR spectra. So, you can see here again it is quite extensive I have given for almost all element starting from ^1H to here this much. And here I have given NMR frequency of 400 megahertz (MHz) for ^1H , the corresponding field strength for various other nuclei can be seen here. And this is an ideal table keep it very handy when you are using NMR. ^2H is here you can see ^7Li lithium is there ($I=3/2$). Lithium is also quite important because we use lithium in many reactions, coupling reactions and other things. In order to see reaction pathways and other things, we can also do variable temperature NMR and understand how lithium is reacting or how lithium is coming out during the reaction. And ^{13}C , I have given for example, 400 megahertz (MHz) what is important is ^{13}C shows about 100, almost 1/4 times and then if you go for ^{19}F it is 376, and then phosphorous NMR will be 161 and then platinum selenium.

So, these are the very important ones ^1H is 400 megahertz (MHz) and corresponding for ^{13}C is about 100 megahertz (MHz) and then corresponding ^{19}F is 376 and then ^{31}P is 162 and if you go for 500 megahertz (MHz) phosphorous (^{31}P) will be about 200 megahertz (MHz). So, magnetic dipole moment μ in units of nuclear magneton will be given in this equation here where M_p is the mass of a proton. If you want to calculate magnetic dipole moment μ for whatever the values are given here what you need is these things if you know the mass of a proton, rest all are constant, you should be able to calculate. So, this is the typical NMR spectrometer here shown. So, the magnet is there which gives B_0 I was telling you. So, here the sample is kept in a soft glass container and then the magnetic controller is there, magnetic field is adjusted here, what you do, the magnetic field you are applying perpendicular, all these things come in this one and then the information goes to detector and to radio frequency transmitter from there.

So, detector will show you about absorption of energy and then you get the plot here very nicely. You can get a spectrum clearly depending on the chemical shifts and coupling constants if there are any and of course, here field strength is increasing. These values are given in delta (δ) chemical shifts that is ppm. So, when you are referring to chemical shift either use delta or ppm one of that one will do. So, let us look into a simple molecule and look into ^1H NMR. So, I have given here for methanol. So, in methanol I would say these are here more shielded observe at a higher field and here less shielded observed at a lower field.

So, that means, here why it is observed at a lesser field and why they are observed at a higher field can be seen here. So, depending on their chemical environment, protons in a molecule are shielded to different extent depending upon their chemical environment. If you see here, oxygen being more electronegative push the bonded pair between H and O in such a way that it becomes almost like H^+ . So, in this case what happens, you do not have really electron density surrounding H to generate an induced magnetic field opposing the applied magnetic field. That means, whatever the magnitude of the induced

magnetic field generated is very minimum, as a result the actual magnetic field experienced by H in this case is same and hence is less shielded.

Whereas, here that is not the case; each one is surrounded by electrons and these electrons generate a magnetic field opposing the applied magnetic field; as a result, they are shielded and observed at a higher field. So, now, let us look into the NMR signals. So, the number of signals shows how many different kinds of protons are present. For example, if you look into ^1H NMR spectrum of ethanol we get 3 signals when we get 3 signals that indicates that there are 3 different kind of protons are present, we know that it is because of CH_3 group CH_2 and OH . So, now, the location of signals shows how shielded or deshielded the proton is first information is how many groups are there and next one is where they are appearing in the NMR spectrum.

The location of signals also indicates whether they are shielded or deshielded and then the intensity of the signal shows the number of protons of that type. That means, all this vital information you can get it one is number of signals and then where they are located and then what are their intensities. That means, basically if we have $\text{CH}_3\text{CH}_2\text{OH}$, we have CH_3 should have higher intensity ok, equivalent to 3 hydrogen atom CH_2 have little less having for 2 hydrogen atoms and then what the ratio of intensity should be 3 is to 2 is to 1. So, that information also comes from NMR. So, this all this vital information we can get simply by looking into NMR signals.

The signal splitting shows the number of protons is adjacent atom. Now, where they are located after identifying 3 groups the relative positions of those groups in the molecule should be very vital to understand the whole molecule. In that case what happens the signal splitting shows the number of protons on adjacent atoms. So, that would indicate where exactly they are located. So, all this information now comes from NMR signals.

So, one is number of signals; how many groups are there and then the location of the signal shows whether they are shielded or deshielded, the intensity would show the

relative number of protons present and then the signal splitting shows where they are located whether they are close to each other; whether they are farther from each other; all these information comes. With this 4 vital information, we should be able to write the molecular structure without any ambiguity. So, all this information comes from NMR signals. So, now let us look into the NMR spectrum of methanol here. Methanol has 2 type of protons one is CH₃ protons one is OH proton and you can see as I said OH proton is less shielded and it is appearing here for this one and whereas, methyl protons are more shielded they are appearing here and then if you look into the intensity this correspond to 3 hydrogen and this corresponds to ¹H hydrogen. So, if I take something like this 1, 2, 3.

So, you can tell very easily and this is the increasing field strength where they are appearing. So, all this information whatever the 4 points I mentioned in the previous slide all this information is nicely depicted in this spectrum. This is the strength of NMR spectroscopy. You can see here the signals, all 3 are identical. So, that means, now all are resonating at the same frequency because all are identical and then this comes at 4.3 this is the value is 4.3 and this is 3.48.

So, now, let us look into tetra methyl silane (TMS). In case of TMS, 4 methyl groups are surrounding the silicon atom in a tetrahedral fashion and this one is added to the sample, while measuring ¹H, ¹³C and also ²⁹Si. Since the silicon is less electronegative than carbon TMS protons are highly shielded signal defined as 0. That means, here relatively compared to carbon, the electronegativity of silicon is less. The protons present in tetra methyl silane are highly shielded and the signal defined as 0. So, the resonance where it comes in the spectrum is given the value of 0 and, we are measuring the chemical shifts of rest of the molecule with respect to 0 value of TMS.

So, this is used as a reference. So, organic protons absorb downfield to the left of the TMS. Most of the organic molecules we come across always absorb energy and they appear left side of the NMR spectrum. So, compared to this one the Larmor frequency is more, why? Larmor frequency is more because they are highly deshielded compared to TMS. So, now, let us look into the chemical shifts. So, chemical shifts whatever the

signals I showed you they are called chemical shifts for example, methanol I showed you two chemical shifts two signals one for oxygen bound hydrogen other three for carbon bound hydrogen.

So, these signals are called as chemical shifts and they are measured in parts per million and they are the ratio of shift downfield from TMS to total spectrometer frequency. Why we measure in parts per million is this unit is independent of magnetic field strength. If I say 3.48 for methyl protons in methanol whether I measure NMR or record NMR spectrum at 60 megahertz (MHz), 100 megahertz, or 300 megahertz it remains the same; that is the reason we measure that in ppm. So, same value for 60 megahertz (MHz), 100 megahertz (MHz), 300 megahertz (MHz) or 500 megahertz (MHz) machine call the delta scale we call it as delta scale here we call it as delta scale.

So, let me stop here and continue more discussion on chemical shifts to make you familiar with different types of chemical shifts and how they are influenced why we call it as chemical shift in the first place. This information let me discuss in more detail in my next lecture. Until then have an excellent time reading on interpretive spectroscopy. Thank you. you