Hello students, today we are going to study NMR spectroscopy with respect to its principle an how NMR spectroscopy is used for finding out the structure of organic molecule.
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We are going to study this particular topic under Industrial chemistry in semester five with paper code ICD 101 with the paper title Industrial Chemistry Analysis. The module number is 4 and the module name is NMR Spectra of simple compounds and the problems.
Under this, you're going to come across some terminologies like equivalent and non equivalent protons, chemical shift, reference standard, shielding and de shielding effect. Up field and downfield signals, anisotropic effect, coupling constant and signals splitting..

After learning these terminologies you will understand how to identify equivalent and nonequivalent protons. You will know the meaning of chemical shift and how it is to be calculated. You can find out the reasons for using a reference standard. You can analyze the effect of external magnetic field on various protons in the compound. You would also know the meaning of coupling constant and will try to find out the reason for signal splitting.

When we talk about equivalent and nonequivalent protons, it means the electronic environment around the protons. If it is different, the protons will be nonequivalent.
If the electronic environment is same it is equivalent. Let us take simple example of ethane CH_3CH_3. All six hydrogens are equivalent because the electronic environment around all the six protons is same. If we take a simple example of propane $CH_3CH_2CH_3$. Here there are two types of protons. They are nonequivalent protons because the electronic environment around methyl $–CH_3$ & methylene $–CH_2$ protons is different. They can be easily seen in the graph with different chemical shift.

Now what do you mean by chemical shift? It can be defined in a simple way as change in the positions of the NMR signals due to shielding and de shielding of protons by induced magnetic field. It can also be defined as the displacement of NMR signal from the hypothetical position of maximum shielding. It is denoted as δ and measured in parts per million. When NMR spectrum is taken a reference standard is always used, the reference used is Tetramethylsilane. The reference point from which chemical shifts are measured is the signal from Tetramethylsilane which is taken as zero.

Now, why this tetramethylsilane used as reference standard? There are some reasons In short, we can elaborate them. Tetramethylsilane is chemically inert, doesn't react with compounds whose NMR is to be taken. It is symmetrical molecule which gives single strong and sharp absorption peak due to its 12 equivalent protons. Due to low electronegativity of Silicon, shielding of 12 protons of four methyl groups is greater than in the most of the organic compounds. As a result, most of the NMR signals appear downfield with respect to tetramethylsilane It's a volatile compound having boiling $27^{O}C$ can be easily removed from the sample after taking the NMR and most of the organic compounds are easily soluble in tetramethylsilane.

In presence of the applied magnetic field, when NMR is taken, the circulating electrons generate secondary magnetic field called as induced magnetic field. This induced magnetic field generated can act in two different ways. One in the same direction as that of the applied magnetic field. Then the magnetic field filled by the proton will be increased. It is set to be de shielded. It can act in the opposite direction as that of the applied magnetic field. Then the field failed by proton is less. It is said to be shielded. Shielded proton require higher applied field strength, whereas de shielded protons require lower field string to provide effective field strength at which absorption occurs. Therefor shielding shifts the absorption in the up field region with smaller δ value, whereas de shielding shifts the absorption down filled with larger δ value.

If we take the example of Acetaldehyde .We have what is called as anisotropic effect. If you look at the diagram here, the induced magnetic field generated by circulating π electrons of the carbonyl group oppose the applied magnetic field $H_{O,}$ above and below the carbonyl group, but at the hydrogen it acts in the same direction as that of the applied magnetic field H_o. Due to this, the field felt by hydrogen is more. It is de shielded, hence will require less applied magnetic field for resonance absorbing in the down field region giving larger δ values.

In the NMR, whenever we see intensities of signals and the peak area under that signals which are related to what is called as proton counting. Relative intensities of the peak will be indicated by height of the peak. So more number of protons will give peak with greater height or larger height. More number of equivalent protons. More will be the height or the size of the peak. The height of the peak is proportional to the area under that particular peak. The area under the NMR signal is proportional to the number of protons, giving that signal. The areas under NMR signals are measured by an electronic indicator, which are shown in the spectrum in the form of stepped curves. The height of step curve is equal to the peak area.

This can be explained by taking NMR spectrum of p-tert-butyl toluene. So if you look at this structure you can see we have 9 hydrogens which is shown at the highest peak height. Then we have three hydrogen. The peak height is slightly smaller and then we have also four hydrogens comparable to the peak height. So this diagram explains the stepped curve. Which is appearing in the NMR spectrum

Then, when we talk about signal splitting, if we analyze the Spectra of 1, 1, 2-tri bromo ethane, 1, 1-dibromoethane and Ethyl bromide. Each of these compounds contain two types of protons, but instead of getting two peaks, these Spectra show five, six and seven peaks respectively. This is because the splitting of NMR signals takes place due to spin spin coupling. The signal obtained from each set of equivalent protons appear not as a single signal, but group of peaks due to the electronic environment of nearby protons is referred as spin spin coupling. So in Ethyl bromide here are two types of protons. The signal splitting is taking place the signal because of three hydrogen is splitting into triplet and signal because of two hydrogen is splitting into quartet because of nearby 3 protons.

If we take 1,1-dibromoethane in this case we have signal A because of three hydrogen splitting into a doublet because there is only one hydrogen on the nearby carbon. A signal because of 1 proton splits into triplet because there are three hydrogens nearby.

If we take1, 1, 2-tribromoethane, we have signal A where we have two hydrogen. It splits into double it because nearby carbon is having one hydrogen and signal because of 1 hydrogen indicated in the graph splits into triplet because there are two hydrogens on the nearby carbons.

So, all these analysis can be seen effectively in these reference books. Again, in this organic chemistry by R. T. Morrison & R. N. Boyd is very simple illustrative reference book in which all basic information about NMR is given. From remaining three books you can definitely get more compounds analysis and you can add to your knowledge how to analyze more and more NMR data.

Thank you.