Welcome to the Bachelor of Science third year program, in the subject of chemistry for semester 5 for the course CHC 107, organic chemistry. I am Dr. Durga Kamat from DCT's Dhempe College of Arts and Science and I am going to take up the module on carbon 13 NMR spectroscopy.

The title of the unit is spectroscopic methods in organic chemistry, module name Carbon 13 NMR spectroscopy. Principle of C13 spectroscopy, number of signals, proton coupled and decoupled Spectra.

In this module we will learn about the principle of C13 NMR spectroscopy, difference between C13 NMR and proton NMR spectroscopy, number of signals in C13 NMR Spectra, proton coupled and decoupled Spectra.

At the end of this module you will be able to explain the principle of C13 NMR spectroscopy, differentiate between proton NMR and C 13 NMR spectroscopy, understand the concept of proton coupled and decoupled spectra, identify the number of different carbon environments in an organic compound and indicate the number of signals in C13 NMR Spectra.

C13 NMR spectroscopy, just like proton NMR spectroscopy, is a very useful technique used by the chemist for structure elucidation.
Now let us revise the basic principle of NMR spectroscopy, which will help you to understand the principle of C13 NMR spectroscopy. As whatever you have already learned about proton NMR spectroscopy also applies to C13 NMR spectroscopy.

NMR Spectroscopy is based on the fact that nuclei of atoms have magnetic properties. Some atomic nuclei have a nuclear spin, making them behave like tiny bar magnets. The NMR active nuclei have spin quantum number, I, greater than zero.

NMR phenomenon is limited to the compounds having isotopes with either odd atomic number or odd mass number or both. For example, carbon 12 has I equal to Zero. Also O sixteen isotope has I equal to Zero and they are NMR inactive.

Proton has I equal to half and it is NMR active. Similarly, C13 isotope of carbon has I equal to half and it is NMR active.

In absence of external magnetic field, the magnetic nuclei are oriented randomly. When an external field is applied these magnetic nuclei start precessing at a certain frequency in the radio wave region and can orient themselves in different orientations or 2I + 1 ways. In case of C13 I is equal to half so these nuclei can take up one of the two orientations, one is the lower energy state, aligned with the applied field and the other is the higher energy state which is aligned against the applied field and the difference in energy between these two spin states is equal to h gamma B zero upon two pi, where gamma is the gyromagnetic ratio characteristic for a particular nucleus and measures the strength of the nuclear magnet, whereas B zero is the strength of the applied magnetic field.

The lower energy spin state is slightly more populated than the higher energy spin state. When the compound in an applied field is irradiated with electromagnetic radiation of the proper radiofrequency corresponding to delta E. That is the difference between the two states. A nucleus with alpha spin absorbs a light quantum and is converted to the beta spin state. Thus, when the energy gap between the spin states of precessing nuclei matches the energy of the supplied electromagnetic radiation, absorption occurs and the nuclei are said to be in resonance with electromagnetic radiation.

The resonance frequency in Hertz is dependent upon the nature of the nucleus in question and strength of the applied magnetic field. The high energy nucleus can undergo energy loss, which can be monitored by a radio frequency detector. We've seen that C-12 isotope of carbon is NMR inactive, whereas C13 isotope is NMR active. However, the abundance of C13 isotope is low.

Now let's see the difference between CMR and PMR spectroscopy.The proton nucleus has natural abundance of about 99.98% whereas C13 has low abundance around 1.1%. Similarly, the gyromagnetic ratio for C13 is low. It is 1/4th that of proton gyromagnetic ratio. Both these factors are responsible for poor sensitivity of C13 NMR spectroscopy. Therefore, for weak signals to be observed C13 NMR spectra are scanned repetitively and stored in a computer.

Since the gyromagnetic ratio of C 13 is 1/4th that of proton at a field strength of nine point four Tesla proton comes into resonance at 400 MHz and C 13 comes into resonance at 100.6 megahertz. The common range of energy absorption for C13 is wide δ 0 to 200 relative to TMS, contrasted with δ 0 to 15 for PMR.Thus, fever peaks overlap in C13 Spectra.

This is a C13 NMR spectrum of para methoxy benzaldehyde so let's see this spectrum. Now what do we have to look for in this spectrum? How does CMR Spectra help in structure elucidation? So we need to look at the number of signals, the position of signals or peak and splitting pattern of the peak if any.

The number of signals in C13 NMR Spectra gives information about the number of non -equivalent carbon atoms. The equivalence or non-equivalence of carbons is just the same way as has been dealt with protons. To be chemically equivalent, carbons must also be stereo chemically equivalent. The presence of less number of signals than the total number of carbons present in the molecule signifies presence of symmetry in the molecule. For example, benzene will just give one signal in its CMR spectrum. How many signals do we expect in case of 1, 4-dimethyl benzene? We will get 3 signals because there are three non -equivalent carbon atoms. For ethylbenzene we will get 6 signals because there are six non equivalent carbon atoms. For n-pentane we will get 3 signals. Similarly for propene we will get 3 signals. For cis 2 butene we should get 2 signals. And similarly for trans 2 butene we should get 2 signals.

Position of the chemical shift gives information about the environment of carbon atoms. You will learn more about the position of signals in further module. Splitting pattern of the peak gives information about the number of non-equivalent neighbouring nuclei. So for this we need to look at proton coupled and decoupled Spectra. So first let's see proton coupled Spectra. Natural abundance of C 13 is low. We have already seen so C13-C13 coupling is not observed. Coupling between carbon and hydrogen is strong, and occurs even when they are separated by several intervening bonds. Because of the large J values for C13-H coupling and appreciable values for C13-C-H and C13-C-C-H coupling, proton coupled C13 spectra usually show complex overlapping multiplets that are difficult to interpret. So what is this proton decoupled Spectra? Carbon hydrogen coupling can be removed by a technique called broadband decoupling. In this method, as the carbon spectrum is being obtained, the sample is simultaneously irradiated with a band of radiofrequency radiation that excites all hydrogens. The hydrogens flip rapidly between two spin states, so their two magnetic field orientations average to zero, hence no coupling occurs with the carbon and each peak appears as a singlet at the position corresponding to its chemical shift.

This is the proton decoupled spectrum of para methoxy benzaldehyde. In this spectrum we can see six signals or 6 lines excluding the singlet for TMS absorption, which appears at zero PPM. So these six lines indicate presence of six non-equivalent carbon atoms. The broadband proton decoupled Spectra display write number of signals, that is singlets at proper delta values for the carbon atoms present. However, some valuable information is lost in the process. Whenever the CMR spectrum is run using a technique called off resonance decoupling, the spectrum is simplified and also at the same time some of the splitting information is retained.

Using off resonance decoupling technique, the C 13 nuclei are split only by the protons directly bonded to them and not by any other protons. For example we can see this carbon is not attached to any proton, so in the CMR spectrum, we will get only one signal for this particular carbon. If the carbon is directly attached to one proton, we will get a doublet , if it is attached to two protons, we will get a triplet. If it is attached to three protons, we should get a quartet. And if it is attached to four protons, we should get a pentet. In off resonance decoupling only one bond coupling are observed. So this technique simplifies the Spectra by allowing some of the splitting information to be retained.

This is the off resonance decoupled CMR spectrum of para methoxy benzaldehyde. So we can see here that the methoxy carbon labelled or we have numbered it as six so you can see that methoxy carbon is showing a quartet. Because it is attached directly to three protons. Carbon number 5 and three, they are showing doublets because they are attached to single proton each. Carbon number two and four, they are not attached to any protons, so they will show singlet. Only here the singlet for carbon 4 is merged with the doublet for Carbon number 3, ok and one more doublet we can see for aldehydic proton. OK, we can see that since the carbonyl carbon is attached to a single proton, we will get a doublet. One more example, we'll see. This is the proton decoupled CMR spectrum of secondary butyl bromide. Here we can see that four signals are appearing, excluding the peak for TMS at zero PPM. So we can say that there are four non- equivalent carbon atoms labelled a c d b, but this spectrum does not give us information about how many protons each carbon is attached to. So for that off resonance decoupled CMR spectrum will help us. We can see that the carbon labelled a is attached to three protons, so it will give us a quartet. Carbon labelled c is attached to, two protons, so it will give us a triplet carbon labelled d is attached to a single proton, so we'll get a doublet and carbon labelled b is attached to three protons, so we will get a quartet.

So CMR Spectra help us to give a good picture of the structure of the molecule.
These are the references.

Thank you.