Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture – 08
Nuclear Magnetic Resonance Spectroscopy
Principle and Application in Structure Elucidation
Carbon - 13 NMR

Hello, welcome to module-8 of the course on application of spectroscopic methods in molecular structure determination. In this module, we will consider carbon-13 NMR spectroscopy; just like proton NMR spectroscopy carbon-13 NMR spectroscopy is also a very valuable tool in structure elucidation problem.

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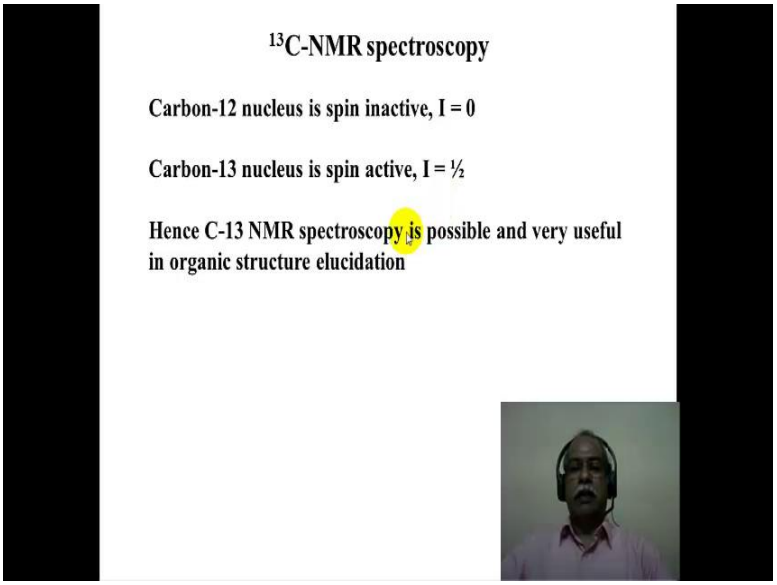

Now, as for as carbon isotopes are concerned carbon-12 isotope has no spin; in other words, it is in spin in active I is equal to 0; whereas carbon-13 nucleus has a spin a half just like proton has a spin of half. Therefore, carbon-13 NMR spectroscopy is possible and it is very useful tool in organic structure elucidation, because it gives a lot of information about the carbon skeleton of the organic compounds.

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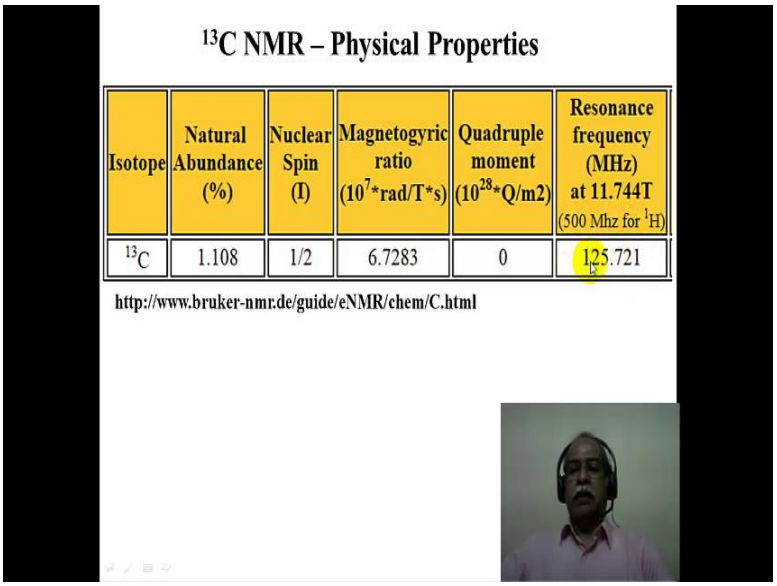

Now, this table gives some important properties of the carbon-13 isotope of carbon. Carbon-13 isotope is low abundant nucleus; it is only about 1.1 percent of the carbon content that is available on earth that is crushed. The nuclear spin is half just like proton the gyromagnetic ratio is just about one-fourth of the gyromagnetic ratio of proton. Proton gyromagnetic ratio is somewhere around 24 something; it does not have any quadruple moment. The gyromagnetic ratio being one-fourth of proton, the resonating frequency is also about one-fourth of the proton resonance frequency. In other words if the proton resonance frequency is 500 mega hertz radio frequency, then the carbon-13 under the same magnetic field strength of about 11.7 Tesla, the carbon will resonate at 125 mega hertz or so.

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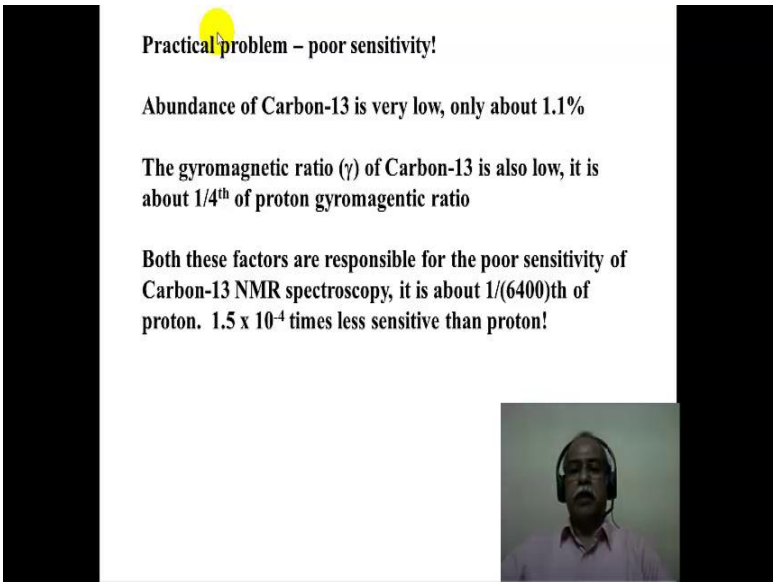

There are several practical problems associated with the poor sensitivity of carbon-13 NMR. First of all it is a low abundant nucleus; it is only about 1.1 percent of the total content of the carbon earth crust is NMR active; the rest in not NMR active namely carbon-12. The gyromagnetic ratio is also low; it is about one-fourth of the proton gyromagnetic ratio. Both these factors are responsible for the poor sensitivity of carbon; therefore, carbon-13 spectroscopy is only about 1 in 6400 of the proton in NMR spectroscopy. In other words, it is about 1.5 10 to the power minus 4 times less sensitive than proton NMR spectroscopy.

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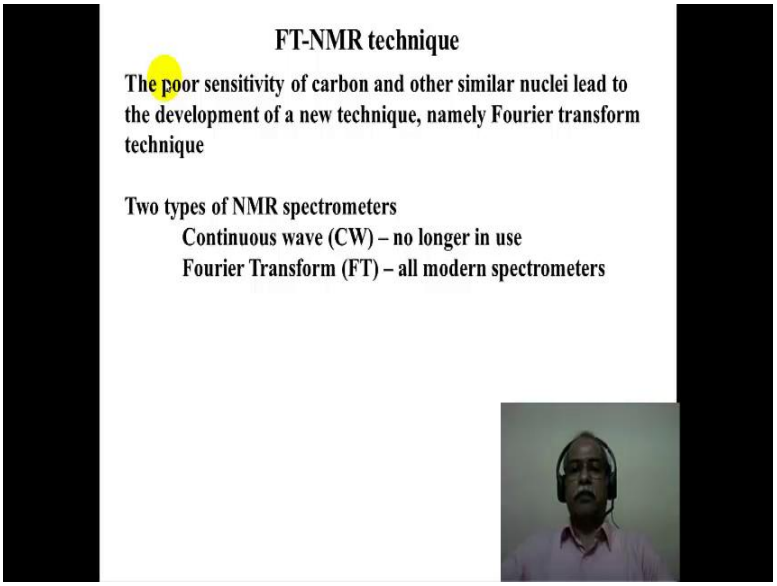

For these reason that is the poor sensitivity of carbon and other similar nuclei which are low abundant and low gyromagnetic ratio, there was a necessity to develop a new technique called Fourier transform NMR technique. There are two type of types of NMR spectrometers are available; one is a continuous wave NMR spectrometer; this is of course no longer in use. Continuous wave NMR spectrometer was the original development of NMR spectroscopy; later on the Fourier transform NMR spectrometer was developed. All the modern spectrometers are Fourier transform NMR spectrometers.

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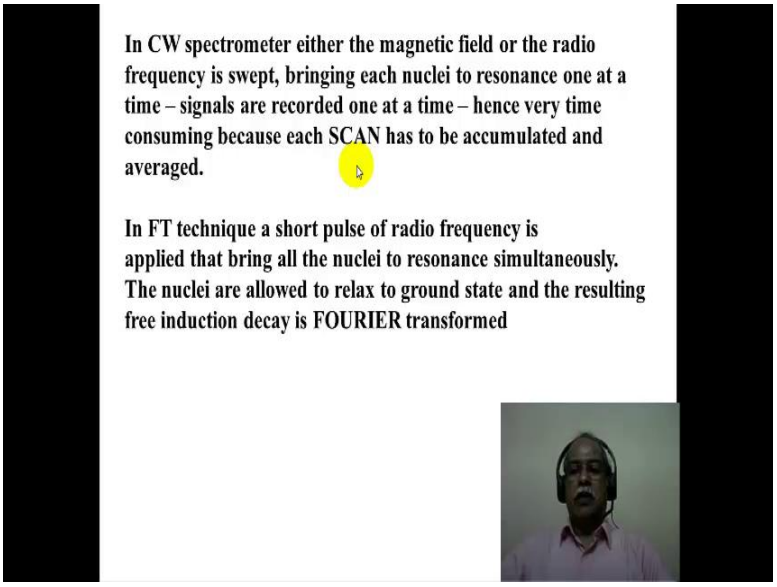

Now, in the continuous wave NMR spectrometer, the magnetic field is scanned and the radio frequency is kept constant. In bringing each nuclei to resonance one at a time, in other words, signals are recorded one at a time by standing the magnetic field keeping the radio frequency constant that is why we says 60 mega hertz. NMR essentially means the operating frequency is 60 mega hertz and the magnetic field strength is vary to cover certain spectral SCAN widths. The continuous wave spectrometer process is a fairly time consuming process, because each SCAN has to be accumulated and averaged. On the other hand, in the FT technique a very short pulse of radio of frequency covering a range of frequency is applied and this brings all the nuclei to resonance simultaneously. The nuclei then are allowed to relax to ground state and the resulting free induction decay is Fourier transformed.

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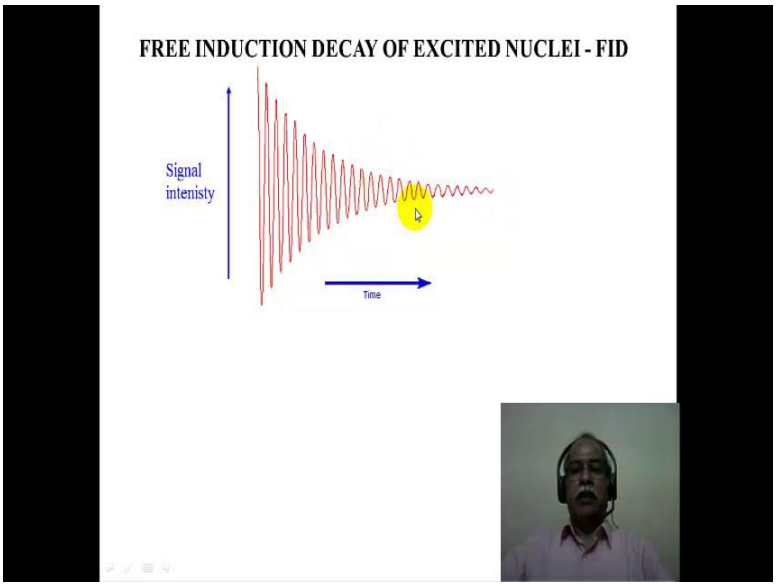

This is pictorially represented here; this is the free induction decay of a single nucleus for example, it is sinusoidal decaying curve is what is shown here. This is the signal intensity versus time; over a period of time then nuclei relaxes back to the ground state indicating the free induction decay of the signal as it is shown in this picture. This is for a single frequency.

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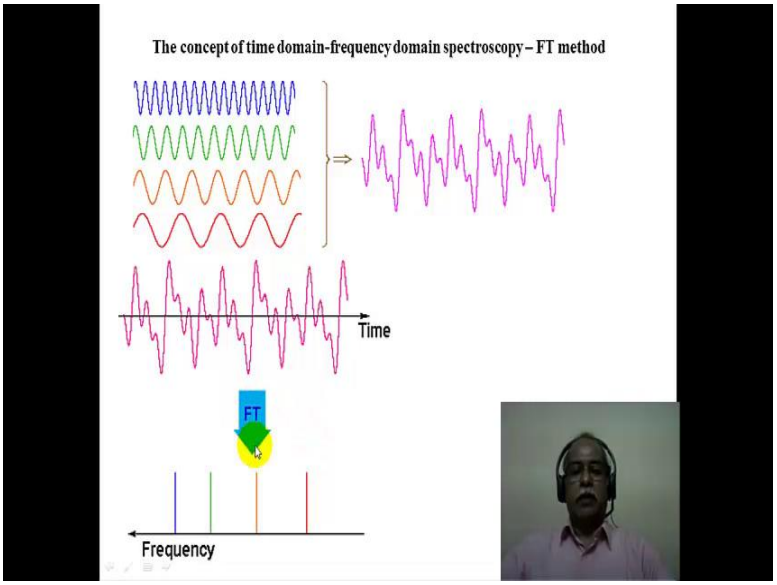

If multiple frequencies are involved then one gets a beep pattern like this involving let us say for example, in this case four different frequency, with a high frequency in the blue

and the low frequency in the magenta color that is shown here. And the time averaged spectrum, the time domain for it is spectrum look something like this with a free induction decay. And when it is Fourier transformed the individual frequencies are sorted out and the process of sorting out the time domain spectrum into a frequency domain spectrum is what is known as the Fourier transformation.

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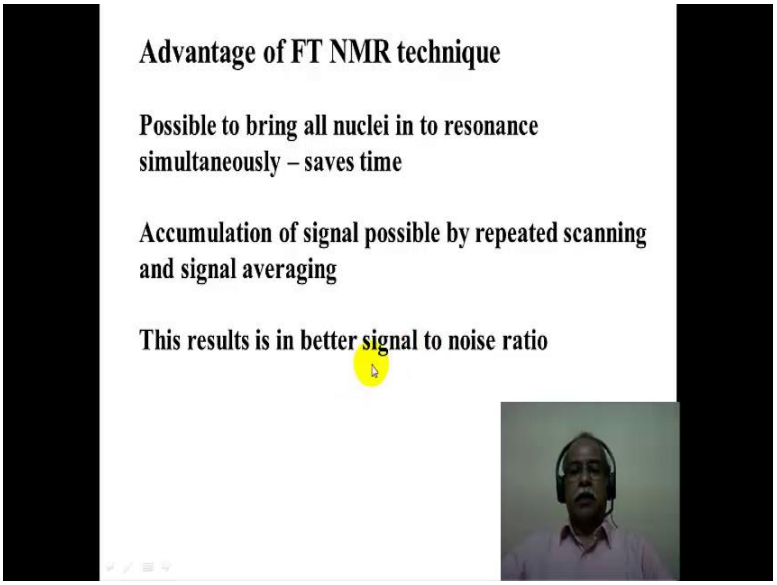

The advantage of the FT NMR technique is that it is possible to bring all the nuclei into the resonance simultaneously; this saves time. Accumulation of signal is possible by repeated scans and signal averaging in a fast way; this results in a better signal to noise ratio.

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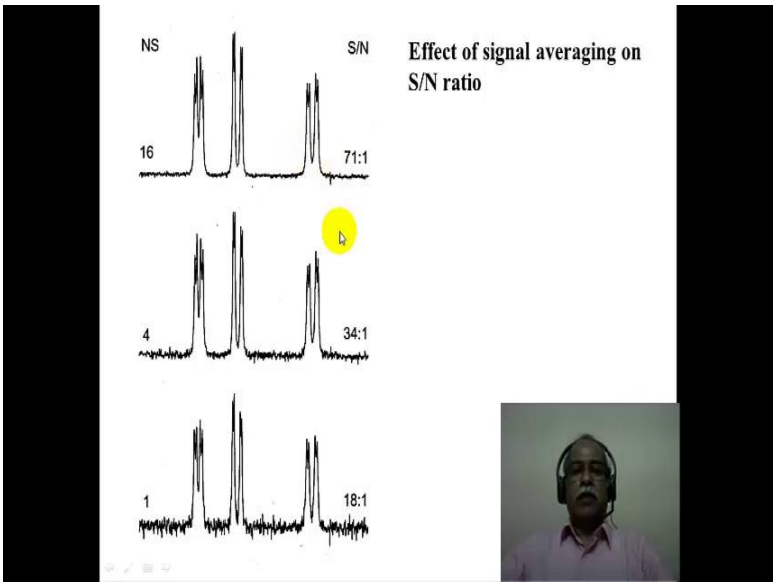

This diagram essentially shows the effect of the number of scans on the signal to noise ratio. We can see here, this is a single scan spectrum; this is an average of 4 scans and this is an average of 16 scans. So, you can see in the base line this is fairly noisy, the signal to noise ratio is 18 is to 1. This is relatively better the signal to noise ratio is 34 is to 1; whereas, this is the dust spectrum among the three in terms of noise being very low the signal to noise ratio is about 71 is to 1. This essentially shows that the more number of scans that one averages the signal gets better noise is random, so it gets canceled out in the averaging process. So, as a result of that you get a better signal to better noise ratio by averaging the spectrum with long number of scans.

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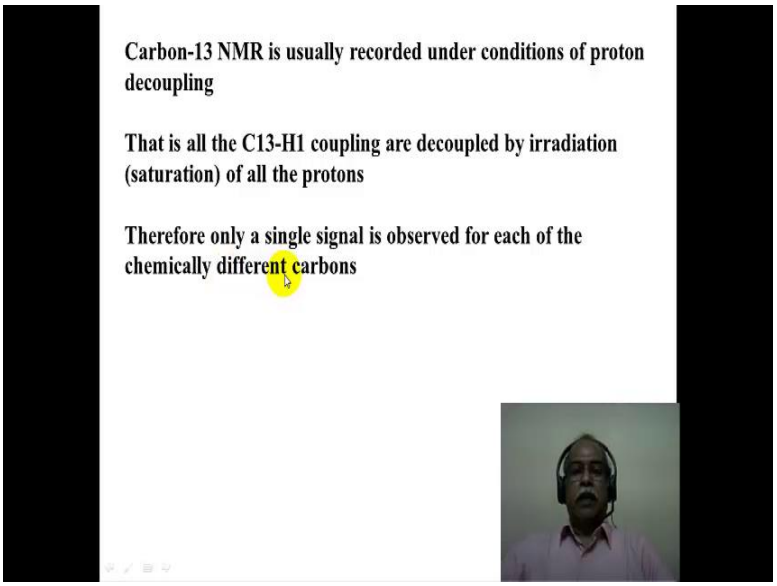

The carbon-13s spectrum is usually recorded under the conditions of proton decoupling. In other words, a separate proton frequency is applied and all the information about the carbon-13 proton coupling is decoupled by irradiation or saturation of all the protons. This is something like a double irradiation experiment except it is a heteronuclear double irradiation experiment; both carbon-13 and proton are simultaneously irradiated, carbon-13 spectrum is observed and proton is decoupled. Therefore, each of the carbon appears as a single line in the NMR spectrum; therefore, only a single line is observed for each chemically different carbon in a carbon skeleton of an organic compound.

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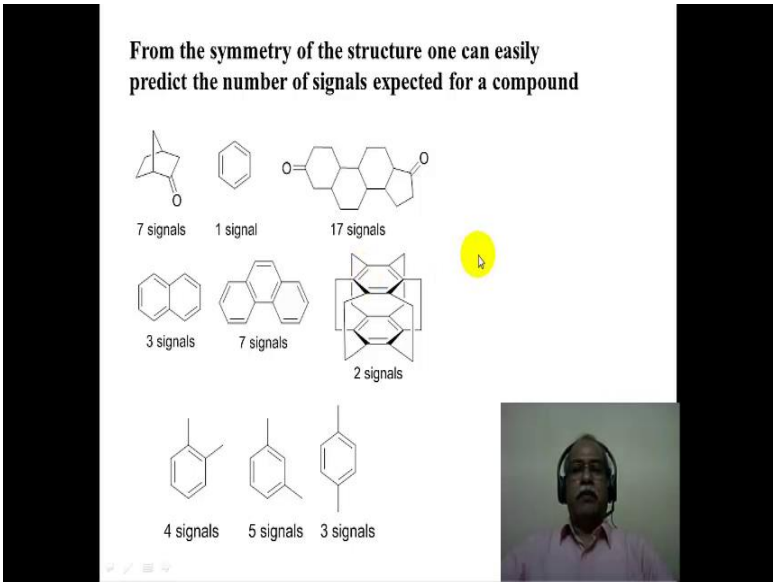

Now, from the symmetry of the structure, one can easily predict the number of signals to be expected for a compound and unsymmetrical chiral compound like this one for example, which contains seven carbons. All the seven carbons are chemically difference. Therefore, one gets seven signals for this type of a compound. On the other hand, the highly symmetrical compound like benzene which has a d 6 h symmetry; all the carbons are equal and chemically identical therefore only one signal is obtained for all the six carbons. This is another example of a steroidal kind of a skeleton with 17 carbons on the skeleton; all the 17 carbons are chemically non-identical they are chemically different. So, 17 signals will be observed for this kind of a compound.

Take this example; this is called super fame, where two benzene rings are connected by a ethylene bridge in all the six carbons around it. This benzene and this benzene are parallel to each other in more or less; and this is a highly symmetrical structure. There are only two types of carbon one is aromatic carbon; all the 12 aromatic carbons namely the six of these benzene ring and six of these aromatic ring are identical. So, it gets one signal one gets one signal for the aromatic carbons, and all the side chain carbons are also identical; all the 12 side chain carbons also give only one signal. So, this is an example of highly symmetrical molecule fairly complex molecule, but highly symmetry nature of this molecule essentially leads to only two carbon signals.

One can easily distinguish the ortho isomer from the meta and tera isomer by carbon-13 spectroscopy, then the two substituent's are identical as in the case of for example, ortho cyclen and meta cyclen and para cyclen as it is represented here. These gives four signals essentially for the two-methyl groups are identical, so it gives one signal. These two carbons are identical, so one signal; these two carbons are identical and these two carbons are also identical. So, it is essentially one, two, three, four because of the planar symmetry that passes through this particular carbon-carbon bond and this carbon-carbon bond.

Here also there is a planar symmetry; the planar of symmetry passes through this carbon and this particular carbon. So, there is carbon one, carbon two, carbon three, carbon four and carbon five; there will be a five distinct signals for five different carbons in this molecule. On the other hand, this has a molecular symmetry planar of symmetry in this direction as well as in this direction. So, there are only two types of ring (Refer Time: 09:49) carbons, the ipso carbon and the ortho carbon. So, this gives 2 signal and the

metal gives the third signal. So, there are totally three signals observed for the paraxylene molecule. So, this essentially tells us that the more symmetrical structure is the lesser number of carbon signals that one would have obtain in an NMR spectrum, the highly unsymmetrical structures will lead to maximum number of signals in a NMR spectrum.

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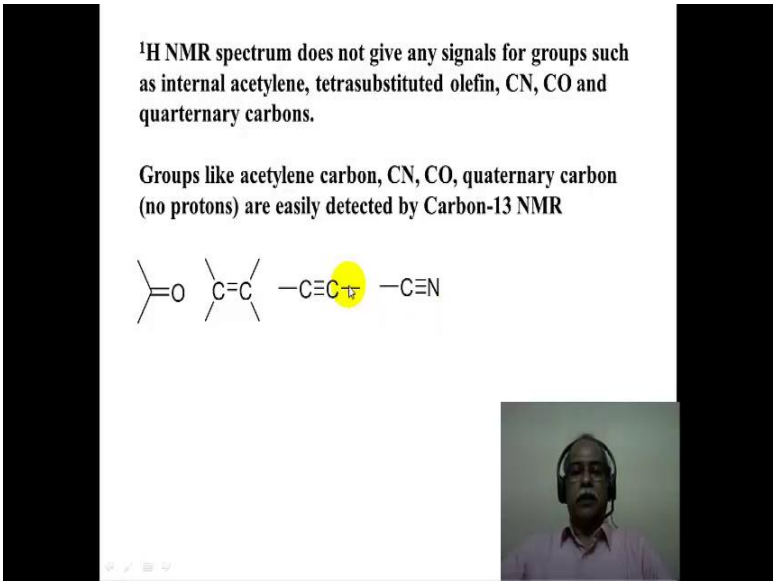

The difference between the proton NMR and the carbon-13 NMR, which is very crucial for structural elucidation is this particular point. In the proton NMR spectrum, one does not get a signal for any of the groups just likes internal acetylene, tetrasubstituted olefin, cyano functional group, carbonyl functional group and quaternary carbons. Now these carbon is do not bare a proton, so there is a proton there is no proton signature in the proton NMR spectrum for any of this groups. On the other hand, in the carbon that in spectrum one gets a direct evidence for groups like acetylene carbon, cyano carbonyl carbon, quaternary carbon and so on. So, these are easily detected in the carbon-13 spectroscopy in comparison to proton NMR spectroscopy where one does not get a one direct evidence for the presence of any of these groups.

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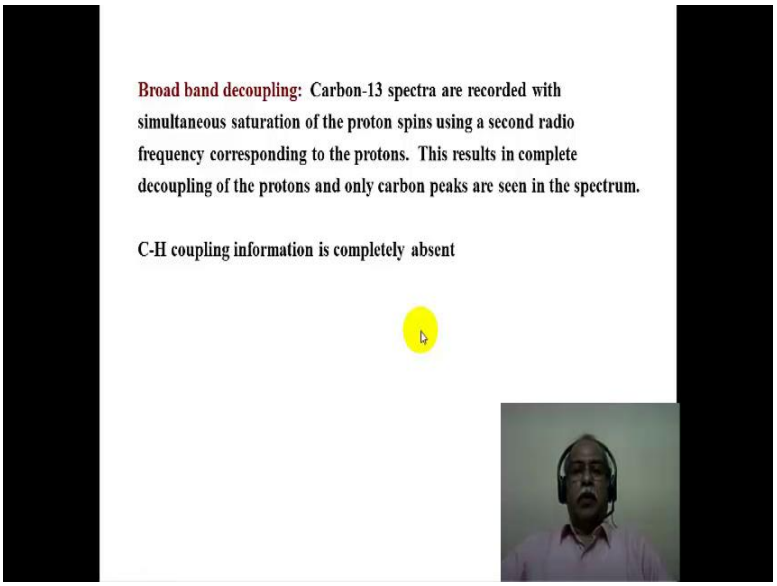

Carbon-13 spectrum is normally acquired on the broad band decoupling mode. In the broad band decoupling mode, carbon-13 spectra are recorded simultaneously with the saturation of the proton spins using a second radio of frequency corresponding to the proton. This result in the complete decoupling of the protons and only carbon peaks are seen in the spectrum and the C-H information coupling information is completely lost or absent in the process.

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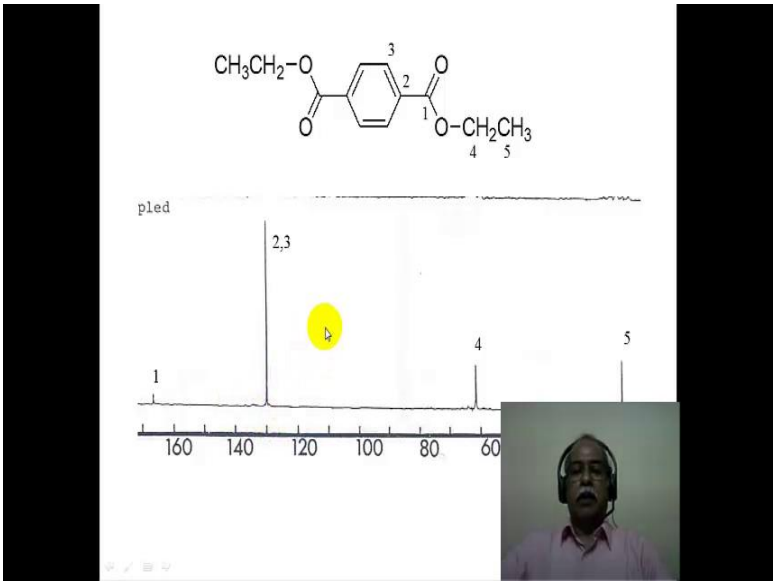

This is an example of a carbon-13 spectrum which is a broad band decoupled carbon-13 spectrum of this particular di-ester. We can see here the carbonyl carbon comes around 169 or 68 ppm. The ipso carbon as well as the ortho carbon namely carbon number 2 and carbon number 3, the accidentally merge in the spectrum they come at the same frequency this is fairly common in carbon-13 spectroscopy, because a narrow region where the aromatic carbons come some of them can be merging on top of each other. Then carbon number 4 comes around 61 or 62 ppm; carbon number 5, which is the terminal metal comes around 15 ppm or so. So from the number of signals that is expected in the number of signals that one sees one can sort of arrive at the molecular structure to be the paradise substitute at derivative in this particular case.

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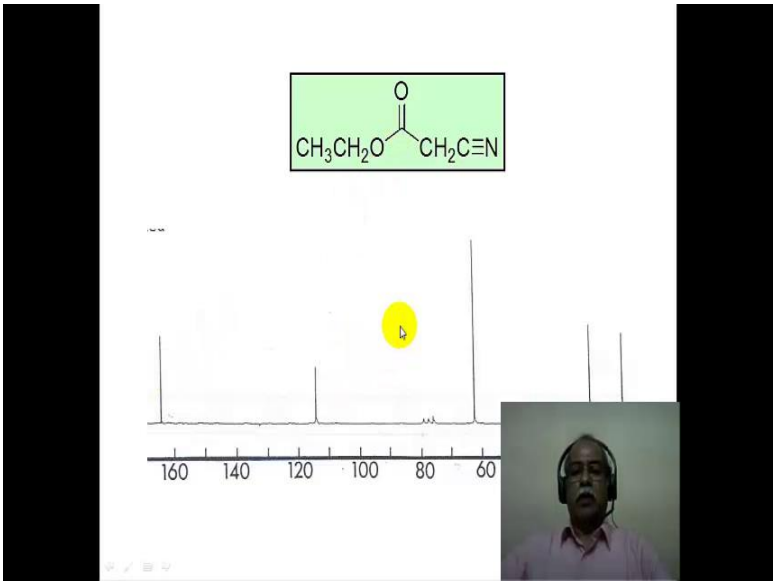

This particular spectrum illustrates the point that the cyano functional group and the carbonyl functional group can be detected in the carbon-13 spectroscopy. Remember we solve the structure of this particular compound using proton NMR spectroscopy and got an indirect evidence that there is a cyano group based on the un saturation index as well as the chemical shift values of this particular proton, which is an indirect evidence that the cyano group is attached to the carbon in this particular molecular. On the other hand, in the carbon 13 spectroscopy get a direct evidence for the cyano functional group, as well as for the cyano functional group in this molecule.

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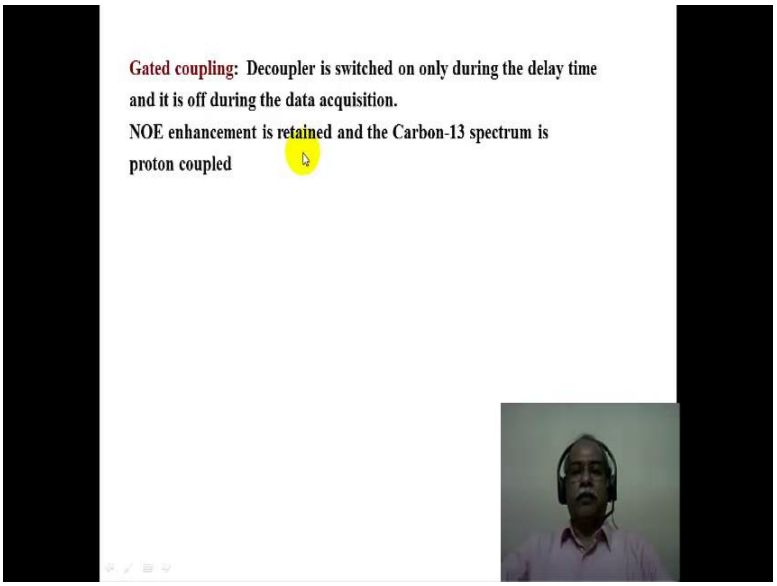

The second methodology that is used in the carbon-13 spectroscopy is called the gated decoupling. We will deal with gated decoupling and the off resonance spectroscopy in much more detail in another module. For the time being, all we need to know use that the decoupler is switched on during the delay time and it is off during the data acquisition. In other words, the carbon-13 spectrum is completely proton coupled; it also has the advantage of the nuclear overhauser effect in enhancement. We will see about the nuclear overhauser effect in much more detail in another module; for the time being, this information is presented essentially for completion.

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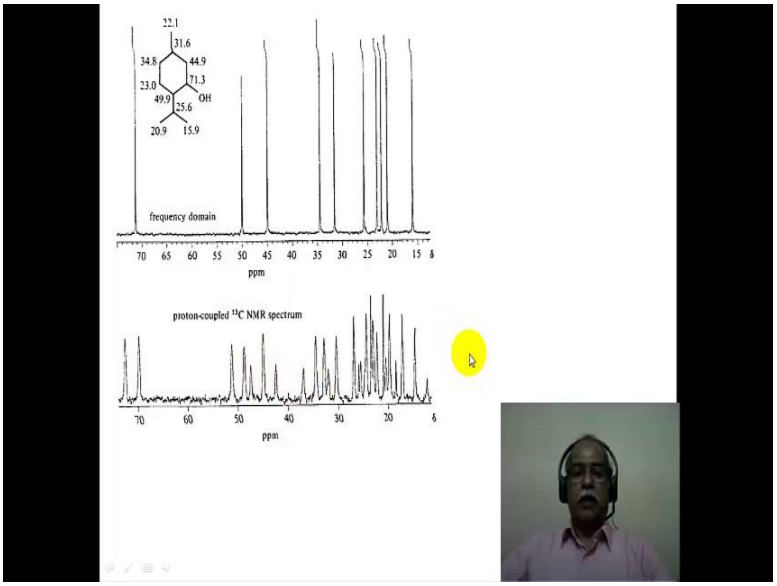

Now if you look at this spectrum, this is a completely proton decoupled spectrum of menthol. Menthol is this particular molecule; and if you look at the number of carbon - carbon 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 signals are there. So, it must contain 10 carbons, 6 ring carbons and one isopropyl 3 carbons are there and another methyl group on carbon, so totally 10 carbons are there in this particular molecule. It is a completely a unsymmetrical molecule it is a chiral molecule. So, another reasons, all the carbons show up separately. The bottom spectrum is actually a proton coupled spectrum, where the C-H coupling information is retained and the spectrum is recorded this is the gated decoupled spectrum and this is broadband decoupled spectrum. In the broadband decoupled spectrum, all the carbon hydrogen coupling information is lost; whereas in the gated decoupled spectrum all the carbon hydrogen information is present coupling information is present; one can analyze the spectrum, although it is a fairly complex spectrum it is possible to analyze this spectrum and obtain the carbon hydrogen individual coupling constraints from this spectrum.

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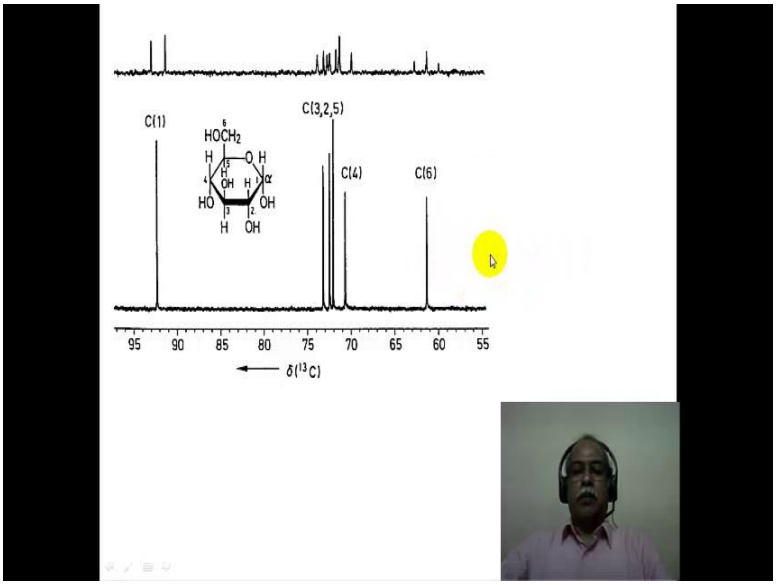

Here is an another example of a gated decoupled spectrum. This is spectrum of glucose for example, and this is a completely proton decoupled spectrum in the bottom trace. In the top trace, you can see it is a carbon hydrogen coupled spectrum. Then a carbon signal is split into a triplet as in the case of the CH 2 OH for example. You can see the intensity of the signal goes down considerably, because this intensity is split essentially into

triplet, so the intensity of the each other peaks in the triplet is much lower than the intensity that one sees in the bottom spectrum.

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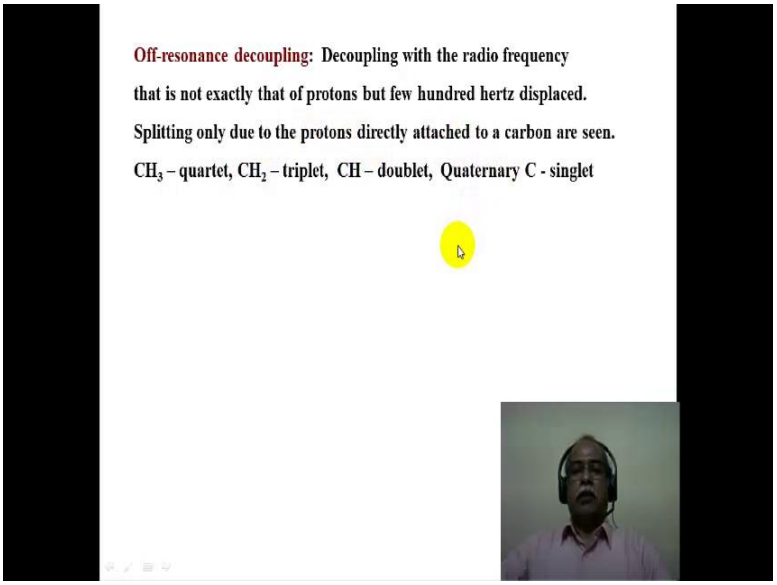

Another technique that is used in the carbon-13 spectroscopy is the off resonance decoupling. The decoupling frequency of the proton is not exactly matched, but it is offset by a few hundred hertz, therefore only the splitting information due to the protons that are directly attached to the carbon are seen here. In other words, when you have a methyl group for example, it will be seen as a quartet in the off resonance spectrum a CH 2 group will be seen as a triplet because the two hydrogen will split the carbon signal into a triplet. The CH kind of carbon like say for example, aromatic carbons, unsubstituted aromatic carbons bearing hydrogen would appear as doublet. Quaternary carbon of course do not have any hydrogen to split, therefore that will appear only as a singlet. So, from the multiplicity one can identify whether it is a CH 3 carbon or a CH 2 carbon or a CH carbon or a quaternary carbon using the off resonance technique.

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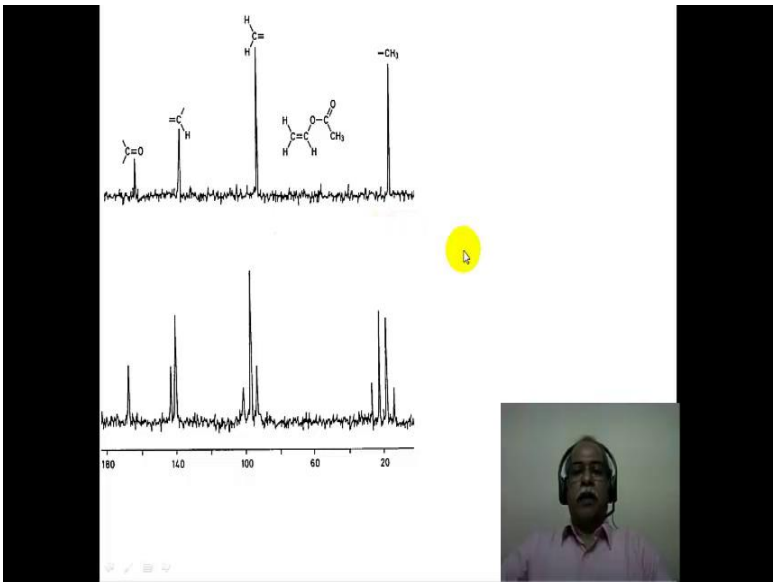

And the off resonance spectrum is presented here for the vinyl acetate; this is a vinyl acetate spectrum. This is completely proton decoupled spectrum. There are four carbons and the four signals are seen; the one for the carbonyl signal, the other one for the internal alkynes carbon, the terminal alkynes carbons comes separately and finally, methyl carbon also comes separately. So, of the methyl carbon now in the off resonance spectrum appears as a quartet, whereas the CH 2 the terminal carbon bearing 2 hydrogen appears as a triplet, although the triplet is a highly distorted triplet not a regular triplet. And the CH carbon of the olefin appears as a doublet, because there is a one carbon attached. Finally, the carbonyl carbon which does not bare any kind of a hydrogen appears as a singlet both in the decoupled spectrum as well in the off resonance spectrum.

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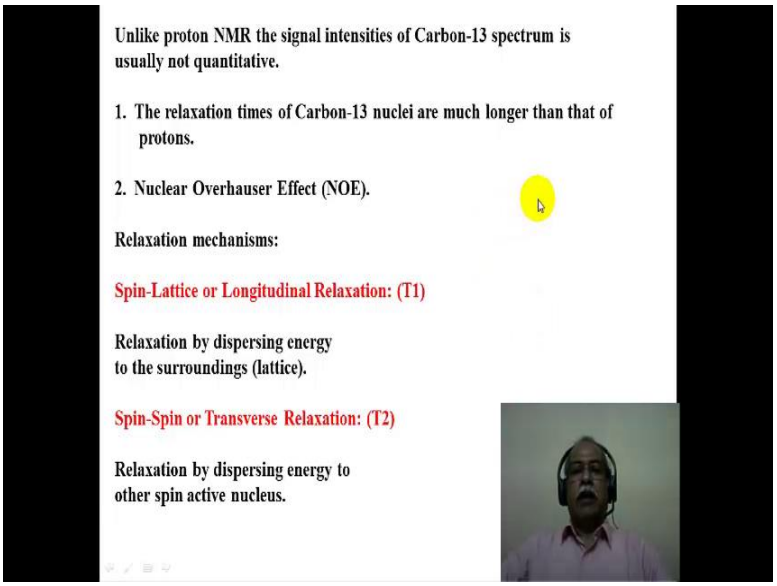

Now, unlike the proton NMR signals which are which can be integrated the intensities can be quantified. Carbon-13 spectrum is usually not quantitative; one does not measure quantitative carbon-13 NMR spectrum. There are two reasons for it, because carbon nuclei have much longer relaxation time. So, it takes a long time for them to come back to the ground state before the second pulse is being applied. So, sometime the signals get saturated in advertently. In addition to that the nuclear overhauser effect also plays the role different carbons have different amount of nuclear overhauser effect or the enhancement due to the nuclear overhauser effect. So, because of these two reasons the signal intensities are not proportional to the number of carbons that are presented in the different chemical environment.

There are two relaxation mechanism by which they excited carbon spin comes to the ground state; one is by spin lattice relaxation or the longitudinal relaxation, and it is designated to the relaxation time is given the symbol T 1. And the relaxation essentially takes place by the dispersion of the energy to the surroundings which is the lattice, it could be a solvent or the surroundings. They alternative mechanism for the relaxation process is a spin-spin relaxation or the transverse relaxation. In this particular relaxation process, the relaxation is by dispersion of the excess energy of the spin to other active spin nucleus is present in the molecule. In other words, for example, if the carbon were to relax, it can pass on the energy to another spin active nucleus like fluorine

phosphorous or hydrogen and thereby it comes back to the ground state by a spin-spin relaxation process.

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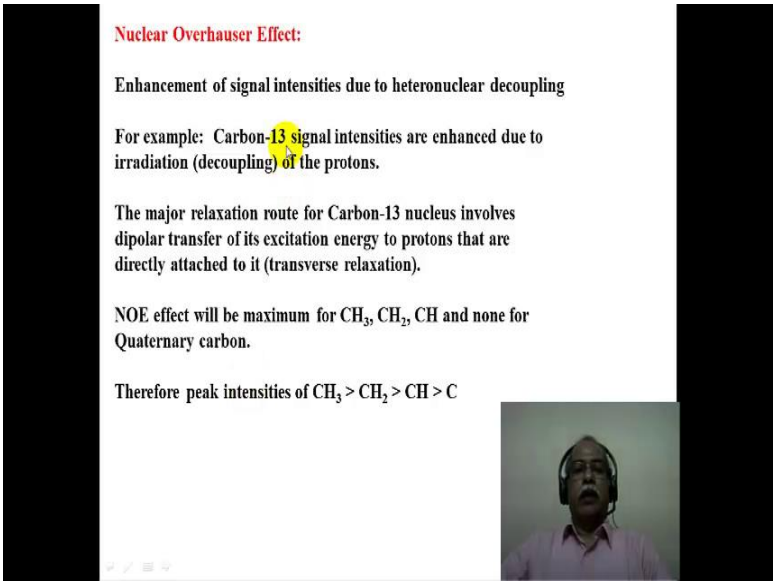

I will deal with the nuclear overhauser effect in a much more detailed manner in another module. For the time being, let us just define, what is the nuclear overhauser effect. The enhancement of signal intensity due to hetero nuclear decoupling is what is known as the nuclear overhauser effect. For example, the carbon that in signal intensities are enhanced due to the irradiation or the decoupling of the protons, because population distribution is different under the conditions of proton irradiation compare to under the conditions of only proton not being a irradiated. This is because the major relaxation route involves dipolar transfer of the excited state energy it is a proton which are directly attach to it each. In other words, the transverse relaxation is what is responsible for the enhancement process that takes place. Therefore, NOE will be maximum for the carbon which has maximum number of hydrogen namely CH 3 and then CH 2 and CH in terms of intensities. Therefore, the peak intensities will be normally CH 3 will be most intense, CH 2 will be the next intense line, CH also will be next intense line. Finally, the quaternary carbons will have the least intensity one can easily identify quaternary carbons in a carbon-13 spectroscopy, because of the poor intensity of that signal compare to the other signals.

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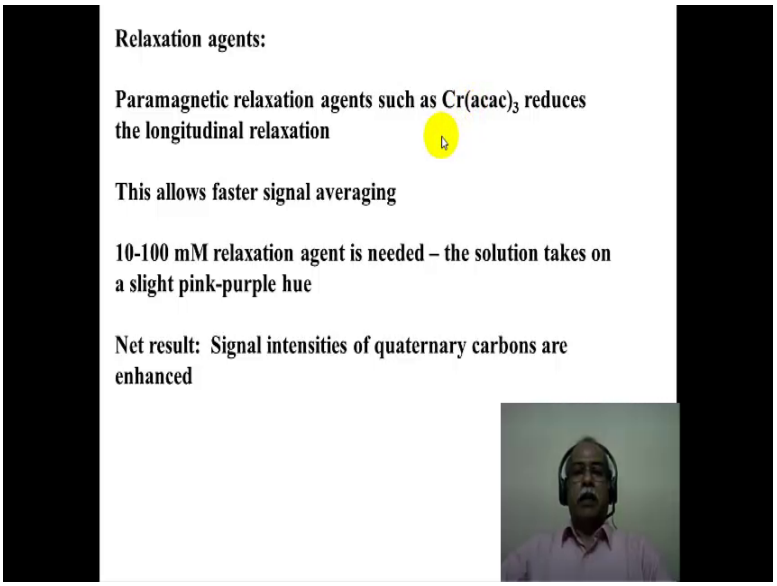

In order to relax the carbon-13 nucleus back to the ground state, there is a technique that is available, where in a paramagnetic relaxation agent such as the chromium acetyl acetones is added. It reduces the longitudinal relaxation period; in other words, it allows the carbon to nuclei to relax much faster; therefore, faster signal averaging is possible, you do not have to wait for the pulses to be given with a long delay duration. Normally about 10 to 100 milli molar relaxation agent is added, when the solution is taken a slight pink color because of the chromium acetyl acetone being a slightly pink color in nature. The result is that signal intensities of the quaternary carbons are now very much enhanced.

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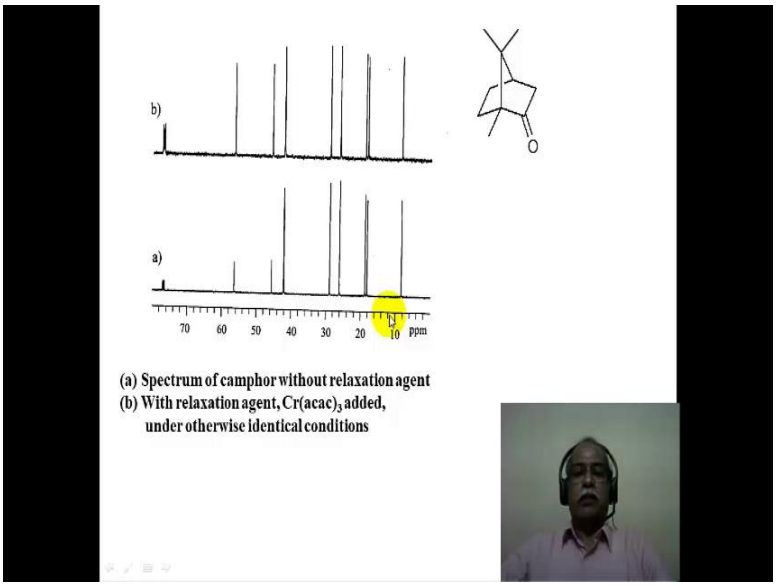

This is illustrated in this picture; this is a spectrum of camphor. This bottom spectrum is without the relaxation process; the top spectrum is with the relaxation agent namely chromium acac being added. The two spectra are identical except top spectrum is along with chromium acetyl acetone which is a relaxation agent. So, you can see here the affect of the relaxation agent. This is the quaternary carbons; there are two quaternary carbons with this molecule; one is this bridge head carbon, the another one is the bridging carbon itself is a quaternary carbon. Those two carbons appear as signals with low intensity with a relaxation agent, of course, we can see that they are signal intensity is much improved because the faster relaxation of the carbon, which comes back to ground state and does not get saturated in the process.

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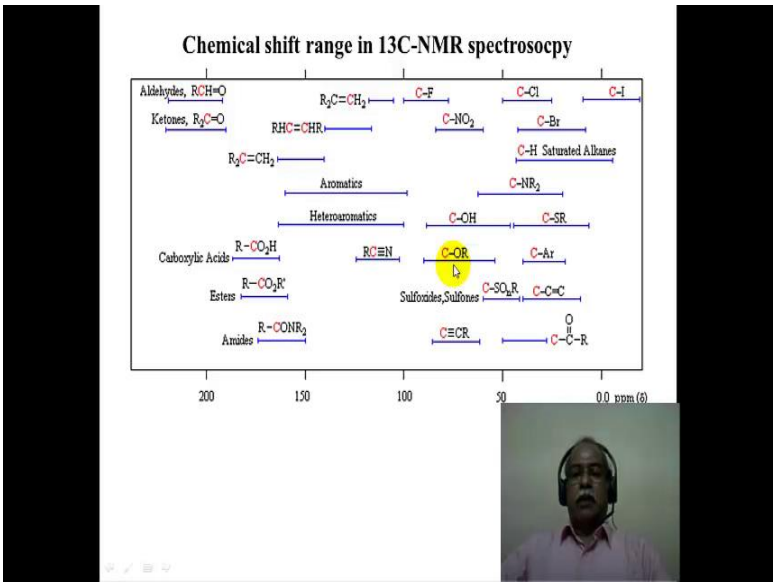

Now, the chemical shift range of a typical carbon-13 spectrum is from 0 ppm to about 220 ppm. Most of the carbons would resonate in this particular range of frequency from 0 ppm to about 220 ppm. And this chart essentially tells what kind of carbons is come and what kind of a chemical shift value. Starting from the higher, and if you look at the 220, 200 region, it is mostly the carbonyl carbons come in the region. Carboxylic acid derivatives come in the region between 160 to 180, or 185 or so. The aromatic carbons come in the region between about 110 to about 140 or 150 depending upon whether you have electron donating substituent or electron withdrawing substituent. Those with the electron donating substituent will be shielded, so they come in the region of 110 or 120, whereas those carbons bearing the electron withdrawing groups like the nitro and chloro and so on they will come in the region between 130 and 140.

Internal olefins carbons are come in the regions same as the aromatic region. In the case of proton NMR spectrum, the aromatic hydrogen come at a higher delta value compare to the olefin hydrogen because of the incongruent affect. In the case of carbon-13, such a incongruent affect is not possible because the carbons do not lie in the shielding or de shielding soon of the incongruent affect that is normally seen. So, the carbons are least affected by the incongruent affect in the carbon-13 spectroscopy. Terminal alkenes come at a lower delta value, sine of functional groups are easily detected they come in the regional between 110 and 120 or 125 or so. The mono substituted derivatives is typically come between anywhere between 20 ppm to about 60 ppm depending upon the electron

negativity of the group that is attached. The most electronegative group for example, the fluorine attached to one will come at around 80 or 90 ppm; whereas, the least electronegative halogen namely the carbon iodine bond for example, that particular carbon comes even in the negative delta value because of the large size of the iodine which completely shields the carbon. So, one has to familiarize this particular table or this particular chemical shift range of carbon that in spectroscopy to be able to solve the structures of organic compounds. It is not necessary to memorize this, but it comes with practice what kind of a carbon will resonate at what kind of a frequency by solving more and more number of problems.

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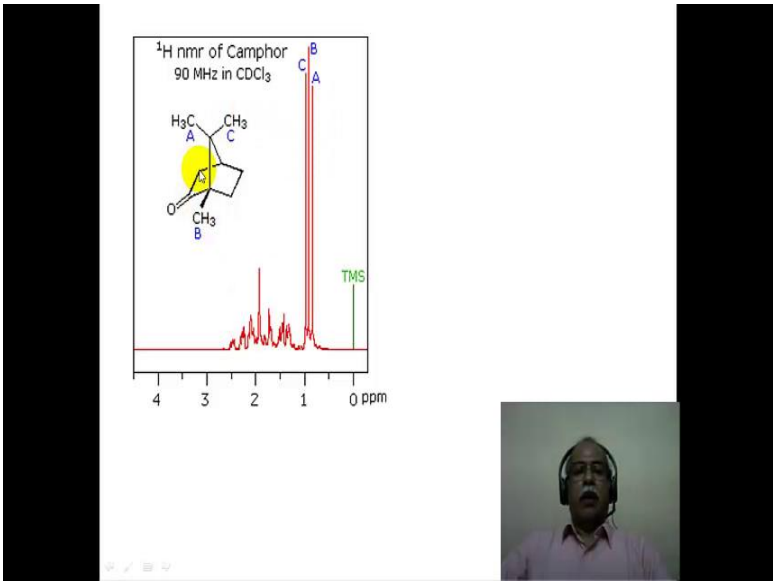

Now, if we look at the spectrum of camphor, this is a proton NMR spectrum. Just to show that the camphor is a completely under solved spectrum except for this two methyl groups sorry the three methyl groups methyl group a, b and c which come separately all the other hydrogen essentially appear as a bunch of signal, unresolved signal in the proton NMR spectrum.

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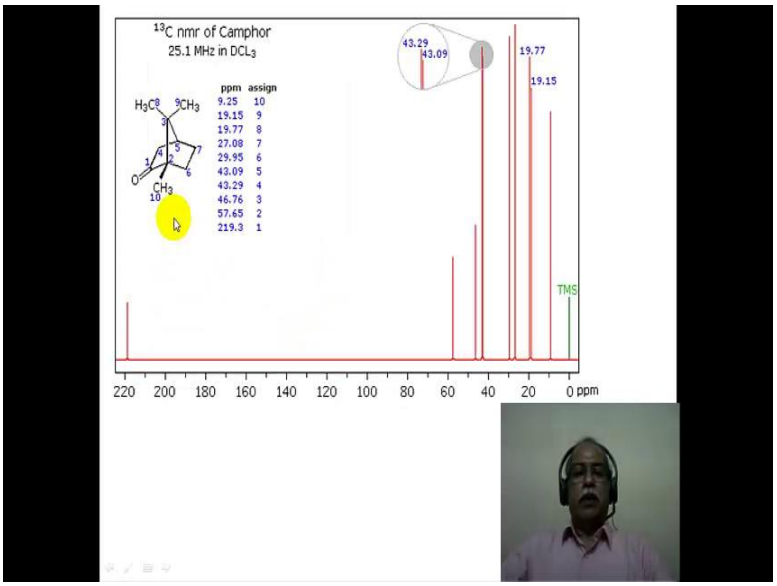

On the other hand, if you look at the carbon-13 spectrum, each one of the carbon comes separately and it is fairly well resolve the spectrum. So, in some sense, the carbon-13 spectroscopy, carbon-13 spectrum is a much more resolved spectrum because of the fact that the individual carbons come at separate frequencies, and the spectral spread is also much higher from 0 to 220 ppm; whereas proton is normally only from 0 to 10 ppm or 0 to 12 ppm or so.

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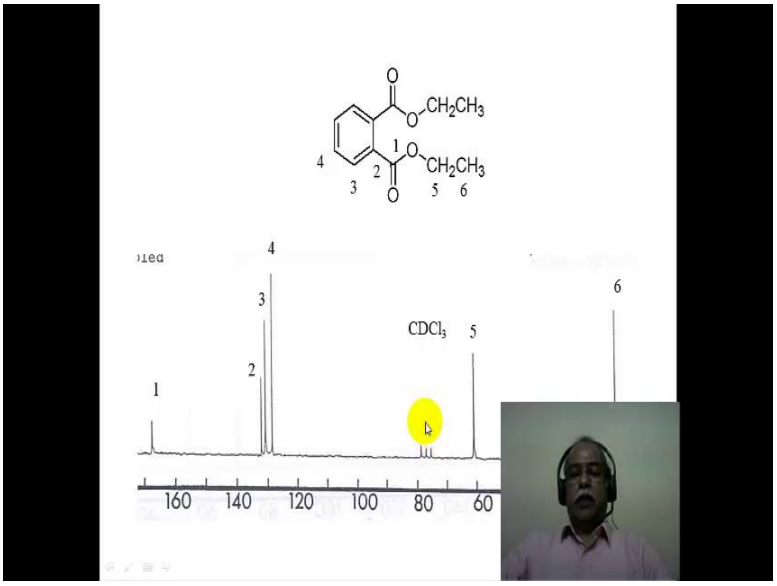

This is a spectrum, which you have already seen this is a spectrum of the diethyl phthalate. There are five different types of carbon in the molecule and one sees five different kinds of signals in the NMR spectrum. Now, when you reduce the symmetry to ortho ester in other words diethyl terephthalate sorry this one is a diethyl terephthalate; whereas this is diethyl phthalate. There is only one plan of symmetry this molecule. So, there are six possible signals that one can have carbonyl signal comes as a the highest delta value around 168 or so. Then comes the ipso carbon which is carbon number two from the intensity itself, one can say that this is a ipso carbon because a carbon intensity is low. Carbon number three and four, which are methane carbon CH carbon the intensity is much higher and these are the two carbons which are three and four for example. And this particular carbon corresponds to the CH 2 and this file, carbon correspond to the CH 3.

If one records the off resonance spectrum of course, the multiplicity will tell which is CH 2 and which is CH 3, but for a simple molecule like this particular molecule simple carbon-13 decoupled spectrum all itself is easily interpretable spectrum. Now if you observe carefully, there is a three-line pattern, which is coming around 77 ppm or so. This is around 77 or 76 ppm. This is because of the solvent peak. Remember solvents also contain carbon which contains carbon-13, so they would also appear in the case of carbon-13 spectroscopy; unlike in the proton NMR spectroscopy when you use the per-deutero solvent, it will not show up in the proton NMR spectrum. But the carbon-13 spectrum will have signatures of the solvent peaks also; this is one such instance where the chloroform peak is seen here. Now this is CDCl 3 peak is what is seen here, essentially you see three lines will a equal intensity because the deuterium couples with the carbon, the deuterium is not decoupled only proton is decoupled. So, the deuterium coupling essentially is deuterium being a spin one nucleus the 2 Ni plus one value corresponds to 3, and therefore, the three line pattern is seen for the CDCl 3.

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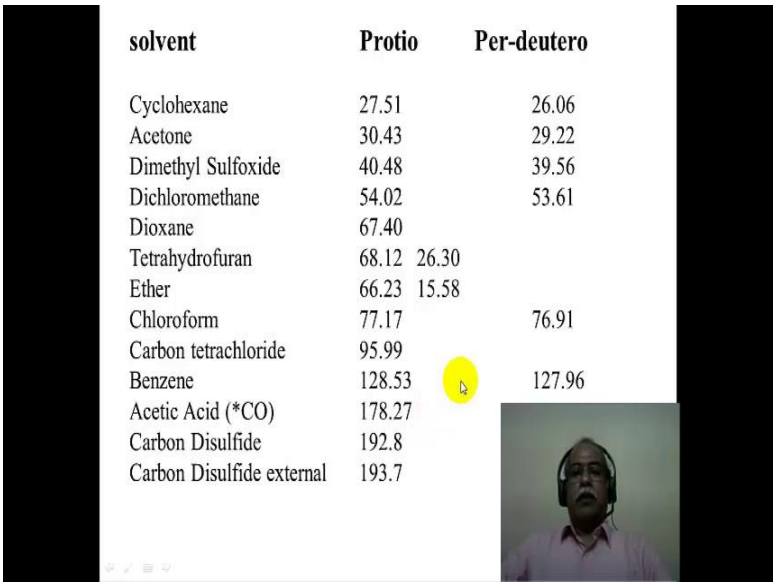

So, just like the CDCl 3 gives this particular spectrum many other solvents also show up in the carbon-13 spectrum. It depends on whether it is a completely protinated cyclohexane 12 protons or cyclohexane per deuterated compound. In other words, you can have a deuterated solvent or a protio solvent. The protio chemical shifts are slightly different from the per deutero chemical shift value; these are the common solvent that one uses for carbon-13 spectroscopy and the resonance frequencies of the protio as well as per deutero solvent is given. Sometimes instead of using tetramethylcylne as a internal reference, the solvent peak is taken as a reference point and with respect to the solvent peak the rest of the spectrum is calibrated.

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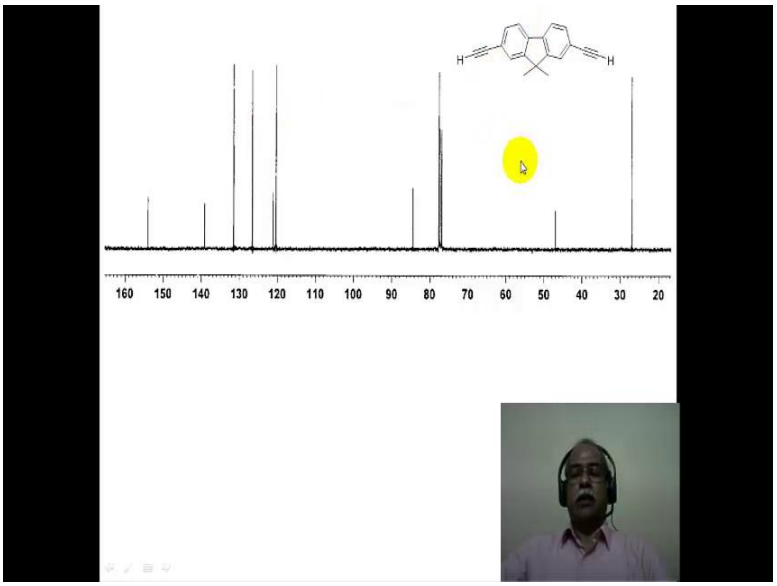

Here is a spectrum of a diacetylene compound this is a symmetrical compound with respect to the planar symmetry passing through this particular carbon bisecting this carbon-carbon bond. So, you need to measure only half the number of carbons in the carbon-13 spectrum, you need to see only half the number. The two methyl groups appear as a singlet as a signal here around 28 ppm or 26 ppm or so. The quaternary carbon, which is as aliphatic carbon comes in this region of 45 or so. In carbon-13 spectroscopy, the more substituted the carbon is the higher will be the delta value and therefore, this quaternary carbons comes here and the methyl carbons which are terminal carbon comes at a lower delta value.

The characteristic signature for these two acetylene peaks are shown here. This is one acetylene peak and this one is another acetylene peak. From the intensity difference, one can tell this is the one which has the hydrogen there was a terminal carbon is see this one the internal acetonlik carbon is this one, and the lines that you see along with the acetonlik ne peaks are this lines due to the CDCl 3 as a solvent here, solvent peak is also shown.

Now if you look at the aromatic region there are two quaternary carbons one can easily find out which are the quaternary carbons; one is here, the other one is here. Remember acetylene has a shielding effect along its axis. So, this particular carbon will be shielded and that comes around 121 ppm, whereas the terminal carbon would come at a much

higher delta value which is sorry the other two carbons not the terminal carbon the other two aromatic carbons would come at a higher delta value. This is one carbon and this is another carbon in terms of the two aromatic carbons, which are quaternary carbons. And finally, the three CH carbons of the aromatic also comes from the intensity we can tell these are the CH carbon which one is rather difficult to say one can calculate based on certain additive rules as to find out what is the nature of this chemical shift of this for this three different CH carbons in this molecule.

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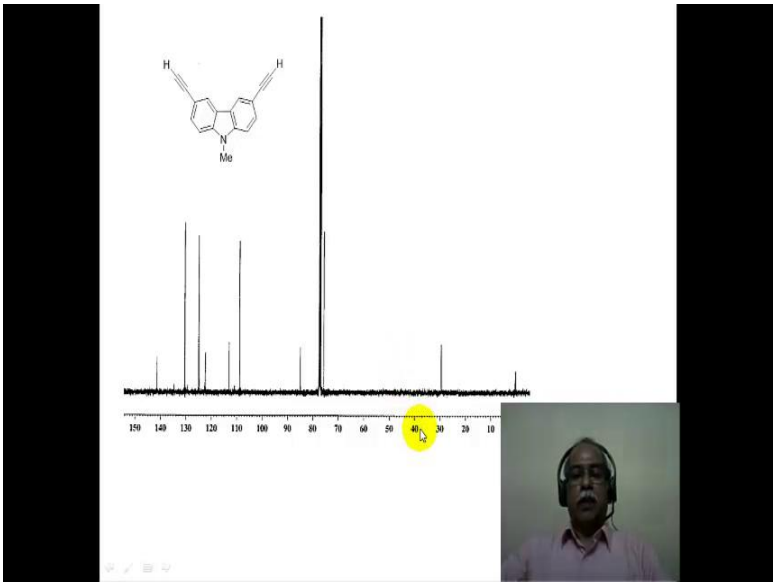

This is another compound, very similar structure except this is a carbosol based structure and this is a fluorine based structure. This also has a planar symmetry passing through nitrogen and bisecting the carbon-carbon bond here. A very similar spectrum is what is seen here there are two acetylene peaks, which are shown here and the n-methyl peak is coming around 30 ppm or so. It is a mono substituted, substituted with a hetero atom that is why it comes around 30 ppm. If it is substituted with an oxygen, it would come around 60, 65 ppm or so. Finally, you have the aromatic carbons six carbons. All the six carbons are seen, because they aromatic ring does not have a any kind of a symmetry, so as a result of that all the six carbons show ups separate peaks out of which three of them are quaternary carbons and three of them are CH carbons which are very clearly identified from the intensity profile of the spectrum.

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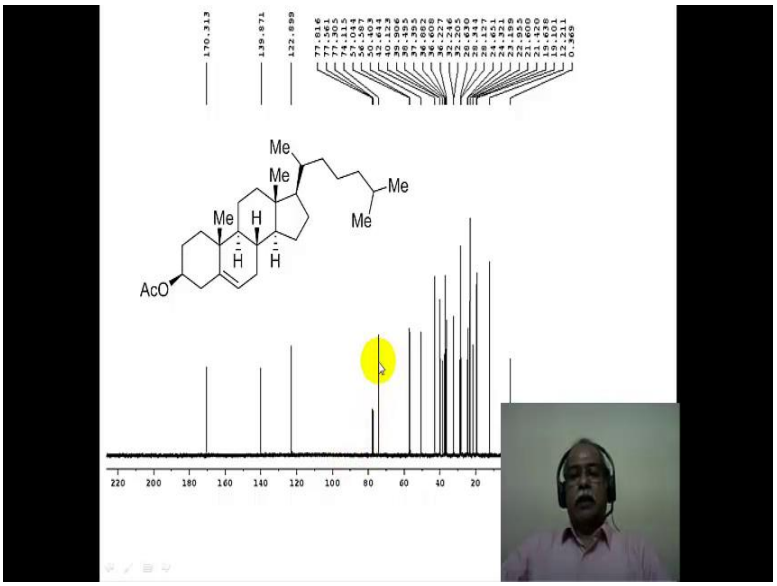

This particular molecule is a steroidal molecule. This is acetate of cholesterol it has about 29 carbon or so including the acetylene carbon. In fact, if one counts the number of signals that is given here, these are the frequency chemical shift values of the various signals that are here. You see about 27 or 29 peaks in this particular spectrum corresponding to the various peaks that can be obtained for this aliphatic compound. Now the most de shielded carbon is the carbonyl carbon of the acetate peak and that comes around 171 or so, so that can be readily identified and the olefinic carbon also these are the olefinic carbons there are only two olefinic carbons which show up in the olefinic region. The more substituted olefinic carbon coming at a higher delta value compare with the less substituted olefinic carbon which is coming at a lower delta value. And this is CDCl 3 peaks three line pattern that you see for the CDCl 3. The rest of the carbons are all because of the skeleton that you have which is basically an aliphatic skeleton more or less a clean spectrum is what is obtained for the cholesterile acetate of this particular spectrum.

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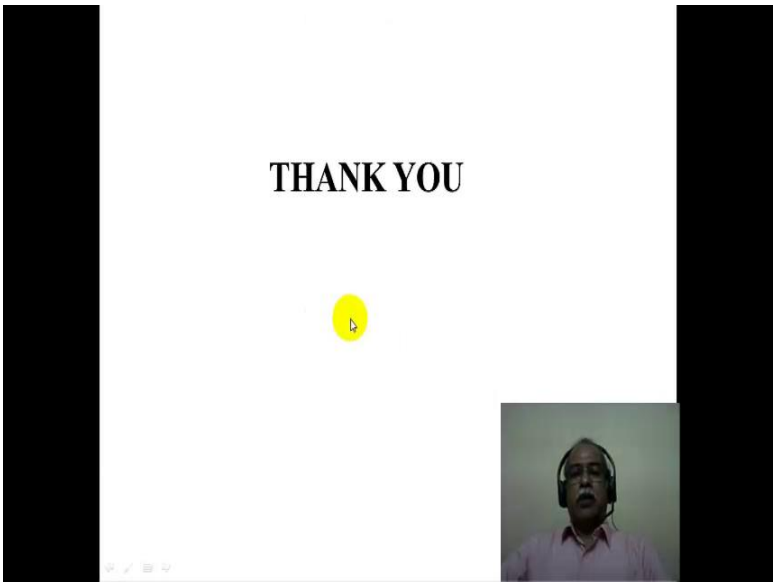

So, what we have seen is an introduction to carbon-13 spectroscopy in this. The various modes of accumulating the carbon-13 information; we had an introduction to the FT technique namely the Fourier transform NMR spectroscopy. Some examples of carbon-13 spectra are also seen in this particular module. In the problems solving session, we will deal with more examples of carbon-13 spectroscopy.

Thank you very much.