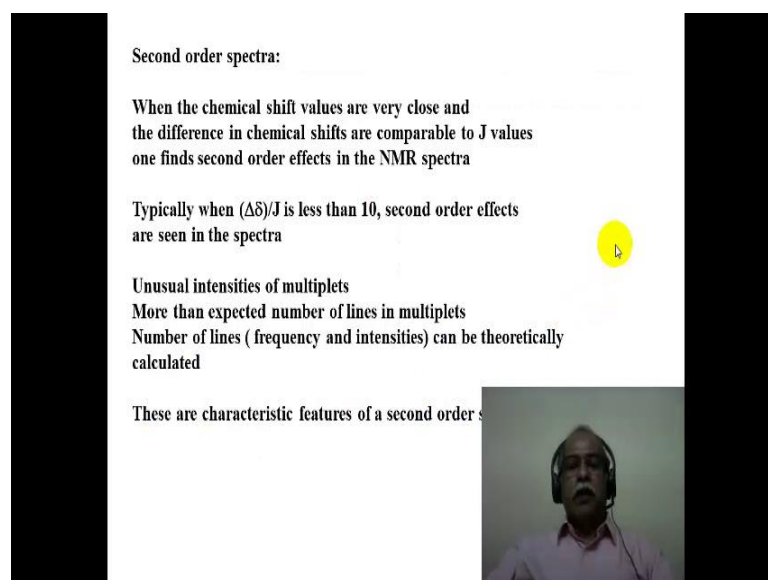**Application of Spectroscopic Methods in**
Molecular Structure Determination
Prof. S. Sankararaman
Department of Chemistry
Indian Institute of Technology, Madras

Lecture - 06
Nuclear Magnetic Resonance Spectroscopy
Principle and Application in Structure Elucidation
Second order spectra

Hello, welcome to module 6 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. In this lecture, we will continue with NMR spectroscopy and have a look at the second order affects in the NMR spectra.

Now, the earlier examples we saw in the previous lectures, the NMR spectra were all simple spectra, in the sense they were all first order spectra and the information about delta value and J value could be directly read from the spectrum itself. It is not always the case that the extraction of delta value and J value in a straight forward manner from the spectrum is possible especially, when a complex second order spectrum is presented.

(Refer Slide Time: 00:54)

Now, let us consider what constitutes a second order spectrum. Consider 2 spins H a and H b, if the chemical shift values of these 2 spins are very close together such that the difference in the chemical shift values are comparable to the J value. One finds second

order effects in the NMR spectrum. Typically, when the ratio of delta delta, in other words the difference in the spectra difference in the chemical shift value of a and b to a ratio of J is less than 10, second order effects are seen in the spectrum. Now, the second order effect is seen as unusual intensities of the multiplet more than the expected number of lines in the multiplet and so on. The number of lines and the frequencies and the intensities can actually be theoretically calculated for any complex NMR spectrum.

These are the characteristic features of the second order spectrum. Namely; the unusual intensities of multiplets and more than the expected number of lines of multiplets in the spectrum.
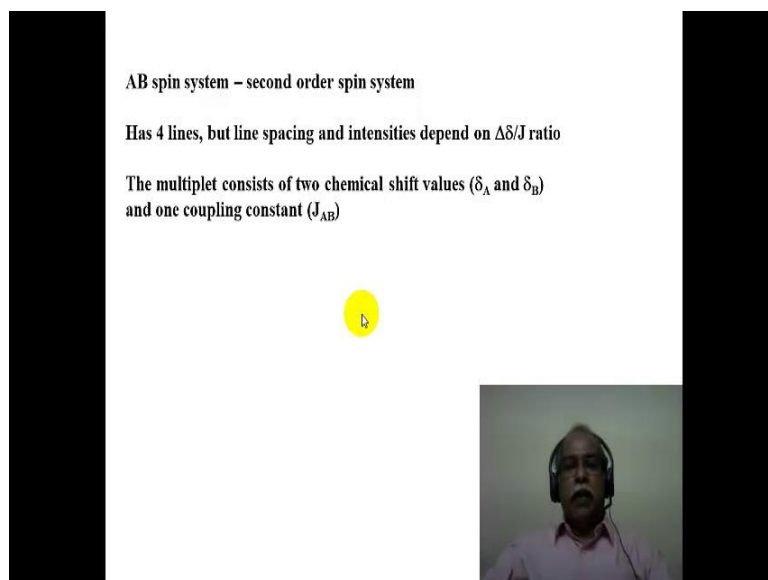
(Refer Slide Time: 01:58)
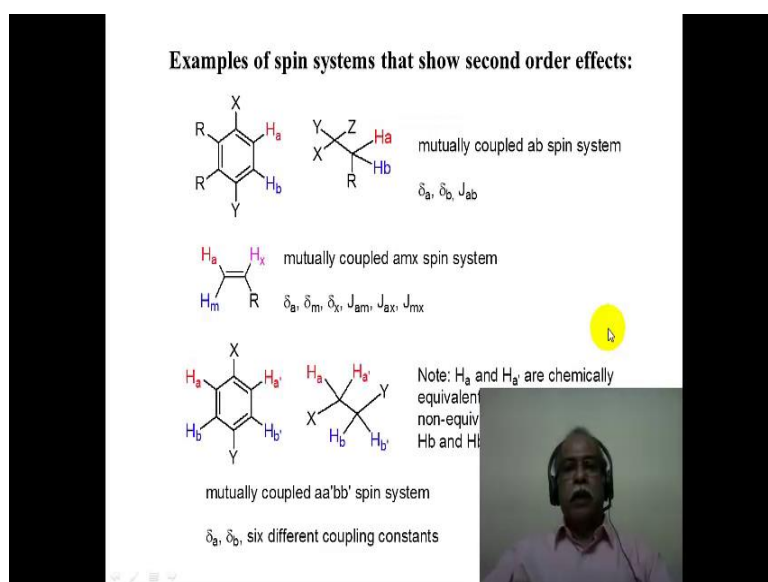
Some examples of spin system that shows second order effects are shown in this particular slide. If we consider aromatic ring, the hydrogens are close in terms of their chemical shift values and normally they are comparable to their J values. So, hydrogen a hydrogen b of this type which is ortho coupled can actually present as second order spectrum which would be an a b spectrum. Consider this example, where the 2 hydrogens are diastereotopic in nature. They may not be very different in their chemical nature. So, their difference in the chemical shift values can be very small and comparable to the J value and that can present an H a b kind of a system, NMR a b kind of a pattern can be seen in the NMR spectrum. Olefinic systems of this type present a very complex

NMR spectrum they can be a b c type or a m x type, depending on the differences in the chemical shift values or various hydrogen which are mutually coupled to each other.

Now, examples of para disubstituted benzene derivative is presented here. That constitutes that AA prime, BB prime type of a fairly complex spin system. So, is this particular disubstituted ethane derivative for example. Depending on the x and y substituent the H a and H b can be very close together in their chemical shift value and that can present a fairly complex NMR spectrum. Typically, alkyl chains or second order the spectrum of alkyl chains are second order in nature and they are fairly complex to interpret. The number of spin system, the chemical shift value and the J value that can be extracted is given in this slide.

(Refer Slide Time: 03:43)

Now, let us consider a 2 spin system, namely, the a b system. In the a b system there are 2 spins and hence 4 lines are expected, but the line spacing and the intensities depend on the ratio of delta delta to J and the multiplet consist of 2 chemical shift value namely delta a and delta b and 1 coupling constant between a and b namely J AB.

(Refer Slide Time: 04:09)
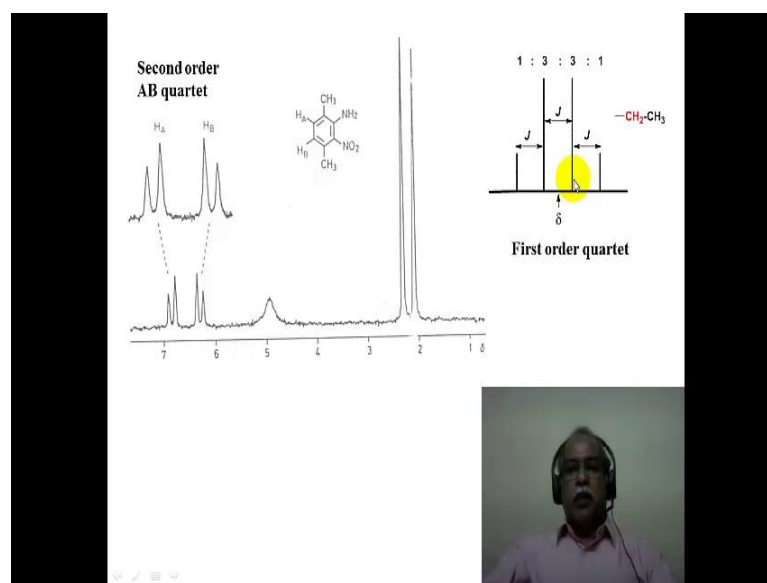
Now, consider the spectrum of this particular nitro amino derivative of para xylene. Now, the 2 aromatic hydrogen are presented here, as H a and H b and they constitute 2 spin system and they appear in this particular pattern. Now, if you look at this pattern carefully H a should couple with H b and split it into a doublet. Similarly, H b should couple with H a and split this into a doublet. So, one should see 2 doublets and the doublets usually should have equal intensities in terms of the 2 lines of the doublet, but that is not the case in this particular system. You can see some kind of a roof effect in terms of the intensity of the inner lines to be higher than the intensity of the outer line, this is a very characteristic feature of the second order effect.

Now, for comparison sake yeah true first order quartet is shown here and this would correspond to something like a CH 2 group of a ethyl group, where you have a CH 2 CH 3 group. Where, CH 2 is typically attached to a hetero atom like an oxygen or nitrogen for example. Under such circumstances the CH 3 splits the CH 2 into a quartet and the difference between this quartet and this quartet is evidence from the picture itself. In this quartet, what you see the AB quartet the intensities are different. The intensities are supposed to be 1 is to 1 for this doublet and 1 is to 1 for this doublet, such is not the case in this particular picture.

And secondly, what is more important is the gap between line 2 and 3 is fairly large compared to the gap between 1 and 2 or 3 and 4. In the case of a simple first order

spectrum, the intensities are predictable it should be 1 to 3 to 3 to 1 and the gap between any adjacent line, would be identical and that represents the J value of the CH 2 CH 3 coupling in this particular case. So, one should not confuse between the second order AB quartet and a simple first order quartet. The differences are highlighted in this particular table.

(Refer Slide Time: 06:10)

First order quartet	AB quartet
All 4 lines equally spaced and the spacing between any adjacent lines is *J* value.	Spacing between lines 2 and 3 varies considerably. Spacing between 1 and 2 or 3 and 4 is *J* value. Spacing between 2 and 3 is not *J* value.
Intensity ratio always 1:3:3:1	Intensity ratios varies widely
Contains only one δ and one *J*	Contains two δ values and one *J*
Spectral pattern is symmetical with respect to center of the multiplet Pattern does not depend on spectrometer frequency.	Spectral pattern is symmetical with respect to center of the multiplet Pattern dependents on spectrometer frequency. Multiplet can look like AB or AM or AX system depending on spectrometer frequency

In the case of First order quartet which is this figure that is shown in the bottom here, all the 4 lines are equally spaced and the spacing between any adjacent line is the J value. Whereas, in the case of AB quartet, spacing between line 2 and 3 will vary considerably, it would depend upon the delta delta divided by J ratio. Spacing between 1 and 2 or 3 and 4 is the J value. Spacing between 2 and 3 is not a J value that is very important to recognize.
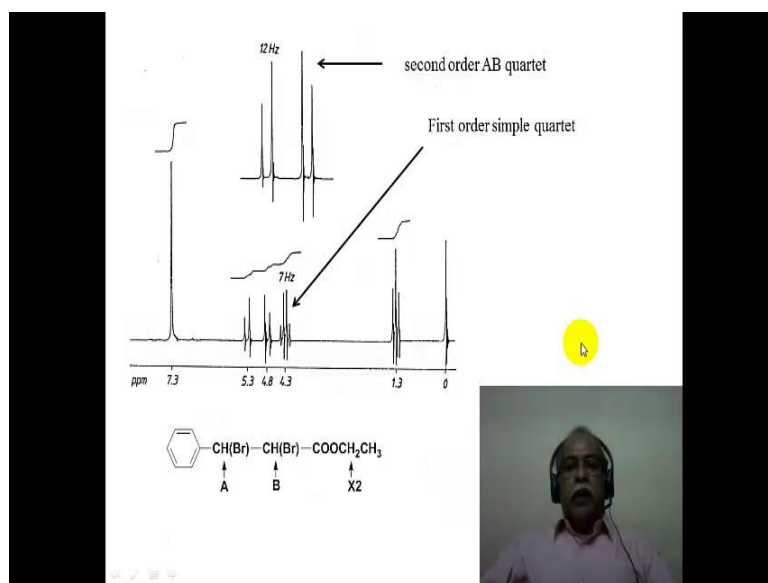
Now, the intensity ratios of a first order quartet will always be 1 is to 3 is to 3 is to 1. Whereas, the intensity ratio of AB quartet will vary widely depending upon the delta delta divided by J ratio.

In the case of a first order quartet, it contains only 1 delta value and 1 J value whereas, in AB quartet actually, it contains 2 delta values and 1 J value which corresponds to J AB. The spectral pattern is symmetrical with respect to the center of the multiplet, what I mean is, if we consider the central point of this AB quartet or the simple quartet on either side of the spectrum with reference to the center point it is symmetrical and that is what

is meant by spectral pattern is symmetrical with respect to center of the multiplet. This is true for both AB pattern as well as the first order pattern. The pattern does not depend on the spectrometer frequency in the case of the first order spectrum. That is extremely important whether you measure it in a 200 megawatt spectrometer or 600 megawatt spectrometer, the line spacing, the intensity and the spectral pattern will look essentially same if it is a first order quartet. On the other hand, AB quartet will depend upon the spectrometer frequency a multiplet that looks like an AB quartet can actually become an AM or an AX type of a system depending on the spectrometer because the delta delta which is expressed in hertz depends on the spectrometer frequency. In other words, the difference in the chemical shift value is expressed in hertz for example, between 2 hydrogen would be dependent on the spectrometer frequency.

So, these are some important differences which are brought out to highlight the difference between the first order quartet and an AB quartet. This is a true second order quartet or AB quartet. You can see it very clearly because of the roof effect. The intensity is not 1 is to 3 is to 3 is to 1 and also spacing between adjacent lines are also not equal in this particular case.

(Refer Slide Time: 08:39)

Now, here is an example of a first order quartet as well as an AB quartet appearing in a spectrum. You consider this dybromo ester, the CH 2 group in the ester functional group is a true first order and that has the intensity ratio of 1 is to 3 is to 3 is to 1 which is

represented by this arrow showing the first order quartet here and between the adjacent lines if you measure the coupling constant, it would correspond to 7 hertz, irrespective of which 2 adjacent lines you take and measure it will always be 7 hertz.

On the other hand, if you consider the benzylic hydrogen which is labeled as A and the adjacent hydrogen which is labeled as B. That constitutes a truly a second order spectrum, AB quartet is what is seen at 4.8 ppm and 5.3 ppm and the expansion of this AB quartet is what is shown in the inset here and with the coupling constant of about 12 hertz this is truly a second order spectrum of AB quartet is what is shown here. Let us see some more examples of AB quartet and familiarize ourselves with the pattern kind of a thing, that we recognize in each one of this spectrum. Pattern recognition is extremely important that makes life easy for the interpretation of the spectral data.

Once again, I should emphasize that in this spectrum what is important is, from the midpoint of the spectrum which is somewhere here on either side of the spectrum, the spectrum looks symmetrical; this is extremely important to recognize.
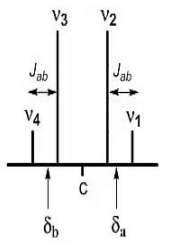
(Refer Slide Time: 10:10)
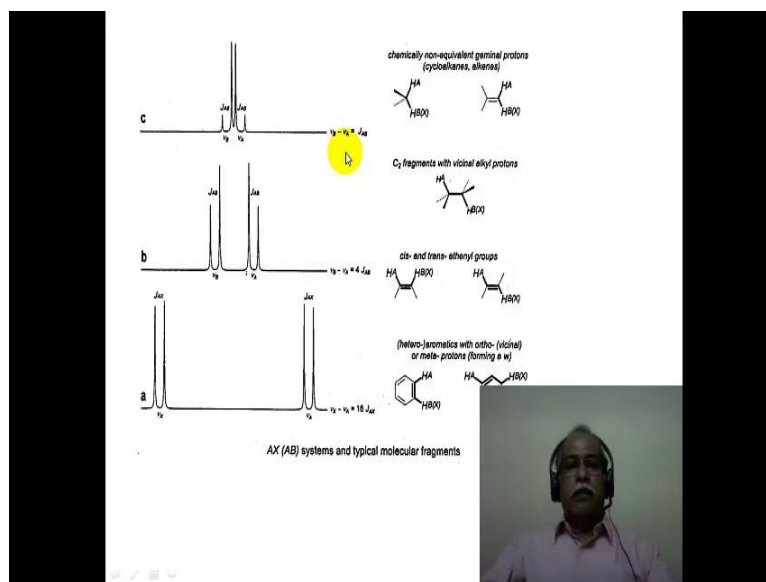
Now, the variation of delta delta with respect to the J value is what is represented here. In the first example, the top example the difference in the chemical shift value is equal to the J value. In the second example, the difference in the chemical shift value is about 4 times the J value. In the last example, which is almost close to a first order kind of a system the difference in the chemical shift value is 16 times the J value. When the

difference in the chemical shift value to the J ratio is more than 10, normally you see a first order spectrum. You can actually see a first order kind of a spectrum, a doublet of equal intensity and another doublet of equal intensity for an AX system.

So, this would correspond to an AB, this would correspond to also an AB system, the last one corresponds to an AX system; AX because A and X are very different in their chemical shift values, that is why 2 alphabets of (Refer Time: 11:07) part is given in the labeling of the 2 spin systems here. Again, once again some examples of the AB kind of a system, you can have diastereotopic methyl hydrogen or you can have geminal olefinic hydrogen for example. You can have 2 hydrogen's on a aliphatic chain adjacent to on adjacent carbons for example. You can have 2 cis hydrogen's or 2 trans hydrogen, ortho hydrogen or meta hydrogen which are all mutually coupled to each other represent an AB type of a system.

(Refer Slide Time: 11:37)

Calculation of δ and J values from a AB spectrum

$\nu_1 = 10.0$ Hz, $\nu_2 = 20.5$ Hz
$\nu_3 = 28.0$ Hz, $\nu_4 = 38.5$ Hz

$\Delta\delta = \sqrt{(\nu_4 - \nu_1)(\nu_3 - \nu_2)}$

$\Delta\delta = \sqrt{(38.5 - 20.5)(28.0 - 10.0)}$

$\Delta\delta = \sqrt{(18)(18)} = 18$ Hz

$c = (20.5 + 28.0)/2 = 24.25$
$\delta_a = (c - \Delta\delta/2) = 24.25 - 9 = 15.25$ Hz
$\delta_b = (c + \Delta\delta/2) = 24.25 + 9 = 33.25$ Hz
$J_{ab} = (\nu_4 - \nu_3) = (\nu_2 - \nu_1) = 10.5$ Hz

$\Delta\delta = \sqrt{(\nu_4 - \nu_1)(\nu_3 - \nu_2)}$

$\delta_a = (c - \Delta\delta/2)$
$\delta_b = (c + \Delta\delta/2)$

$J_{ab} = (\nu_4 - \nu_3) = (\nu_2 - \nu_1)$

Now, how does one calculate the delta value and J value from an AB spectrum? Consider this to be an AB spectrum, one sees 4 frequencies; frequency 1, frequency 2, frequency 3 and frequency 4, labeled as nu 1, nu 2, nu 3 and nu 4. Now, the difference between mu 1 and mu 2 is the J AB or between mu 3 and mu 4 is the J AB. So, the J value can be easily measured from AB spectrum by measuring the difference in the frequency between 1 and 2 or 3 and 4. Now, there is a simple expression which relates the difference in the chemical shift value that is if this is a delta a and this is a delta b

value, the difference in the chemical shift value is represented by delta delta. That is simply given by the expression of square root of nu 4 minus nu one multiplied by nu 3 minus nu 2. So from this, one can actually calculate the difference in the chemical shift value.

When the intensities of the central lines are much taller than the intensities of the line 1 and line 4, it is not the center of the doublet which is the chemical shift value it is a center of gravity of the doublet which makes the chemical shift value, so the chemical shift value actually will be not at the center of this doublet, it will be closer to the taller line in either of the side of the NMR spectrum. Now, once you know the difference between the chemical shift value, this gap that is delta delta once you calculate from this expression you can also calculate the center of the spectrum by taking the average of the frequency 3 and frequency 4. So, frequency 2 plus frequency 3 divided by 2 would be the center of the spectrum. So, one can also figure out the center of the spectrum fairly easily from the spectrum because the spectrum is symmetrical with respect to the center.

Now, simply delta a would then be center of the spectrum frequency minus delta delta divided by 2 and the chemical shift value of b would be simply corresponding to the center of the spectrum frequency plus delta delta divided by 2. The J AB we have already discussed as the difference between line 4 and 3 or the difference between line 2 and 1. Here is an illustrative example, where 4 different frequencies of an AB quartet are given as 10 hertz, 20.5 hertz, 28 hertz and 38.5 hertz. The difference in the chemical shift value is calculated using the simple expression, which corresponds to 18 hertz in this particular case. The center of the spectrum is essentially the average between line 2 and line 3 which is also given as 24.25, all of them are expressed in hertz only. Therefore, the delta a would be c minus delta delta divided by 2, which would be equal to 24.25 minus 9 which is 15.25 hertz.

The delta delta, the delta b would be corresponding to c plus delta delta divided by 2, which would be 24.25 plus 9 which is 33.25 hertz. So, delta a and delta b are extracted from this information in terms of hertz. Now, if you divide it by (Refer Time: 14:46) the spectrometer frequency, one obtains the corresponding values in parts per million. J AB of course, is here 10.5 hertz, which is just a difference between line 1 and line 2 or line 3 and line 4 is about 10.5 hertz. So, an AB quartet is a fairly simple system to analyze, one

can extract information essentially about the delta values and the J value corresponding to J AB from the spectrum.

(Refer Slide Time: 15:13)
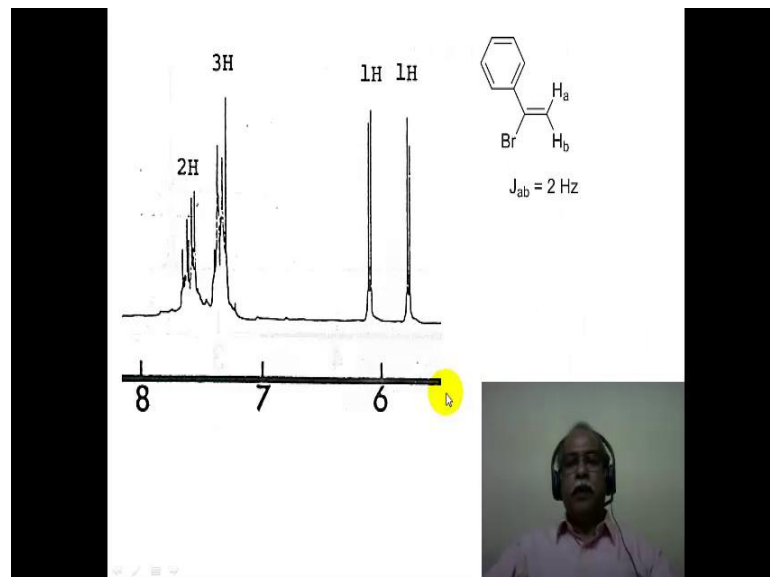
Now, here are some examples of typical a b type of a pattern. This a b pattern corresponds to the 2 hydrogen which are germinal hydrogen attached to the olefinic carbon. Olefinic germinal coupling constant is very small, it is about 2 hertz only. So, you can see a small gap between the doublet and doublet here, never the less, if you look at this particular doublet the 2 lines are of not equal intensity. So, it has a second order effect built in with this.
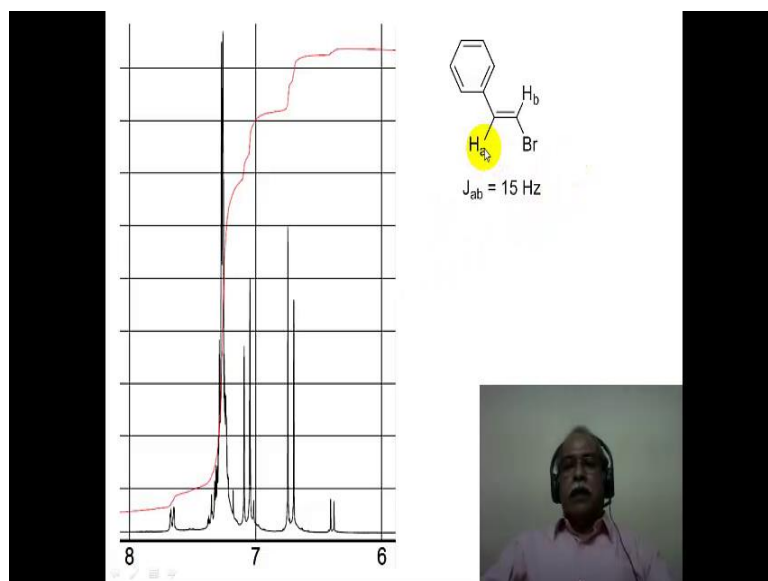
Now, let us consider the trans derivative of the Bromostyrene, Omega bromostyrene. Here also you see a doublet and a doublet corresponding to an a b type of a quartet, with respect to the center of the AB quartet it is symmetrical on either side of the spectrum and hence, this is an AB quartet which can be analyzed like it is shown in 2 transparency earlier.
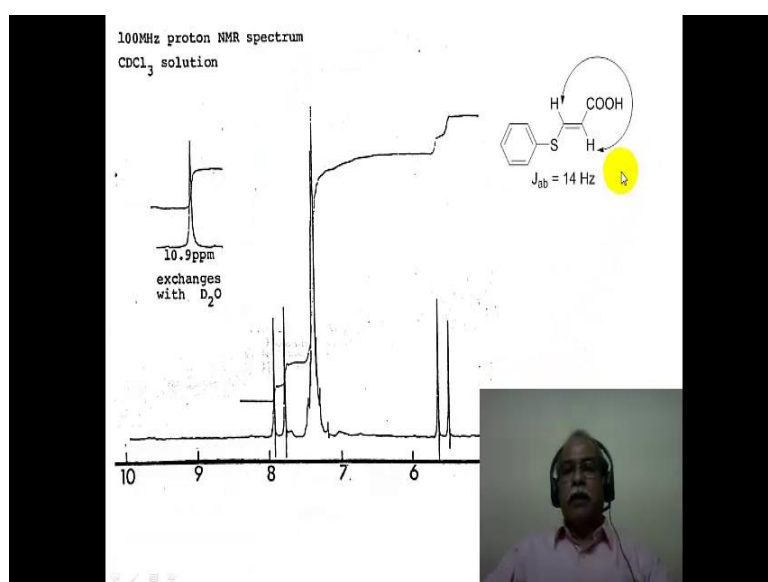
Here is another example of a thio substituted acrylic acid kind of a derivative, where you have a trans coupling between the 2 hydrogens constitute an a b kind of a coupling. So,

this corresponds to essentially an a b pattern. One side of the a b is here, the other side of the a b pattern is here, the center is somewhere here. With respect to the center, again you see a symmetrical pattern on either side of the spectrum.

(Refer Slide Time: 16:30)
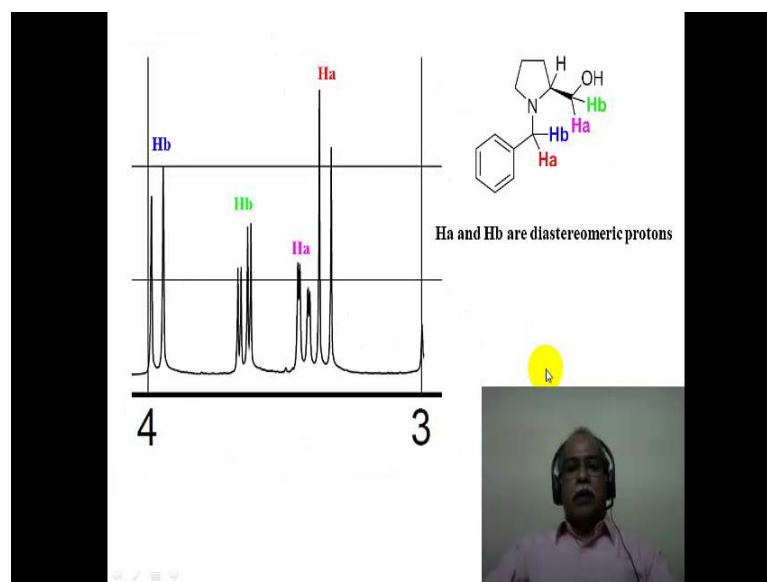
Now, this has 2 types of a b system. The benzylic hydrogens are a b because the chiral center is here, as a result of that these 2 hydrogen's are diastereotopic. The red hydrogen and the blue hydrogen are diasteretopic in nature. And, the red hydrogen one of these hydrogen come at a value of about 3.95 delta or so, which is labeled as H b in this particular case and the H a comes around 3.4 or 3.5 ppm or so, which is somewhere here. So, this is a b corresponding, a b pattern corresponding to the red hydrogen and the blue hydrogen.

There are 2 other hydrogen's, which are magenta hydrogen and the green hydrogen. Which are also forming a b kind of a system, except now this a b is further split into a doublet by this hydrogen. So, AB quartet is split into a doublet. So, you see AB quartet split into a doublet, totally 8 lines is what you are going to see. Again, you have the roof effect kind of a thing, the inner lines are taller than the outer lines on either side of the spectrum, never the less, this could be fairly easy to interpret if you recognize this to be an a b pattern. So, you have 2 diastereomeric pairs of hydrogen a b and a b color coded with different colors in this particular spectrum.

Now, the delta value for the a red and the a b would correspond to analyzing this doublet and this doublet here. The delta value for the magenta a and the green b, magenta hydrogen and the green hydrogen would correspond to analyzing this lines here and this lines here as an AB quartet, which is further split by this hydrogen into a doublet kind of a spectral pattern.
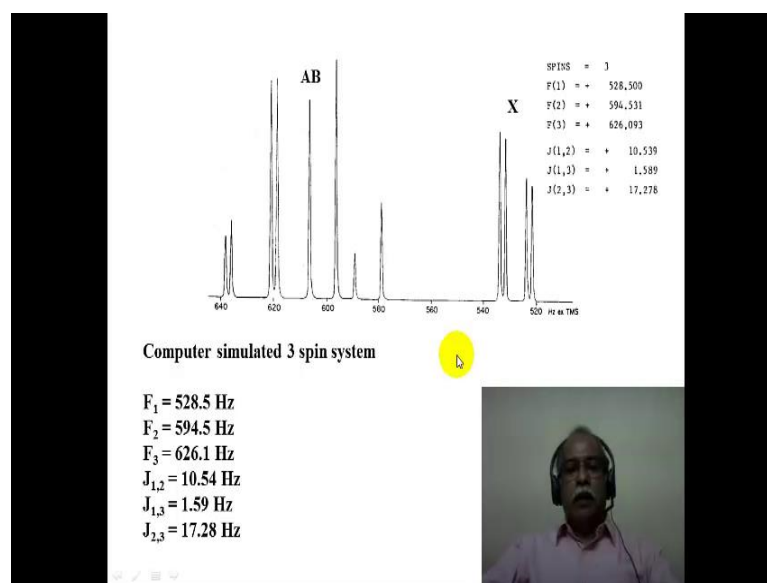
(Refer Slide Time: 18:13)
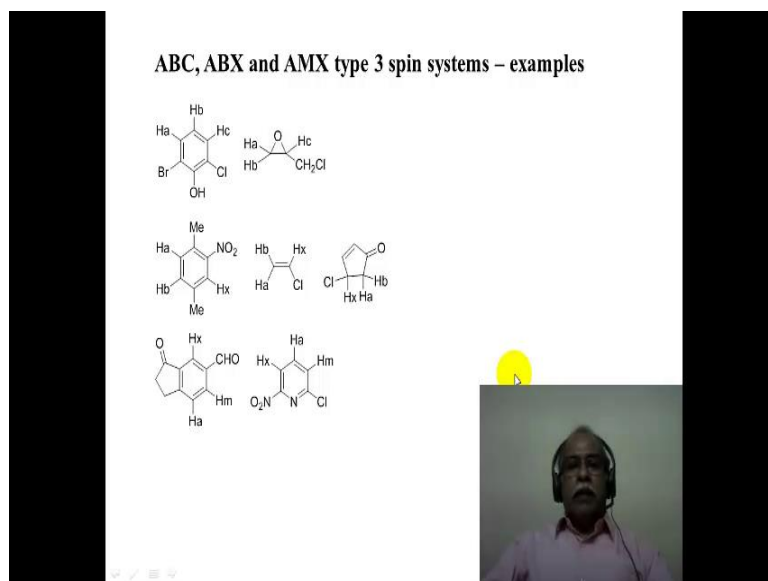
The next higher spin system would be ABC, ABX or AMX, these are 3 spin system, fairly complex systems. Examples of the 3 spin systems are given here in this slide, you can see here for example; a differential ortho substituted phenol this would correspond to an a b system. A allyl chloride epoxide, the epoxide of allyl chloride again constitute us ABC system of the 3 membered ring, the hydrogens on the 3 membered for example. In the case of a aromatic system again, if you consider this derivative which is ortho nitro sorry, 2 nitro para xylene the 3 hydrogens on the aromatic ring would constitute an ABX kind of a system. A mono substituted olefin can present itself a fairly complex spectrum of ABX type for example.

This is another example of an ABX kind of a spectrum and this is one more of ABX. Finally, the pyridine derivative can also present itself as an ABX spectrum, if the 2 substituent in the position 2 and 6 are different substituents. The chemical shift value and the coupling constant values can be different for these 3 types of hydrogen in this molecule.

Computer simulated 3 spin system

$F_1 = 528.5$ Hz
$F_2 = 594.5$ Hz
$F_3 = 626.1$ Hz
$J_{1,2} = 10.54$ Hz
$J_{1,3} = 1.59$ Hz
$J_{2,3} = 17.28$ Hz

Here is a computer simulated 3 spin system the AB part of the spin system is shown separately and the X part of the spin system is also shown separately. Now, these are systems which are typically the olefinic hydrogen, mono substituted olefinic hydrogen where you have AB and an X kind of a system. The X kind of a system is split into 2, one by the J AB other one sorry, one by the J AX the other by J BX. So, one can extract 2 coupling constant information from this spectrum here. And, you can see here the line intensities are not as one would expect for a doublet of a doublet if it were to be a simple AX BX kind of a coupling in this particular pattern.

What one can see of course, is the sort of an AB pattern here, which is further split into a doublet, but the intensities are unusually different in this particular case than what one would expect for a AB, doublet of a AB kind of a spectrum in this particular case. And, the frequency values and the corresponding J values are given, which is used for the computation of these 3 spin system in this particular spectrum.

(Refer Slide Time: 20:42)

Dependence of ABX system on $\Delta\delta_{AB}$

$J_{AB} = 15.7$ Hz, $J_{AX} = 0$ Hz, $J_{BX} = 7.7$ Hz
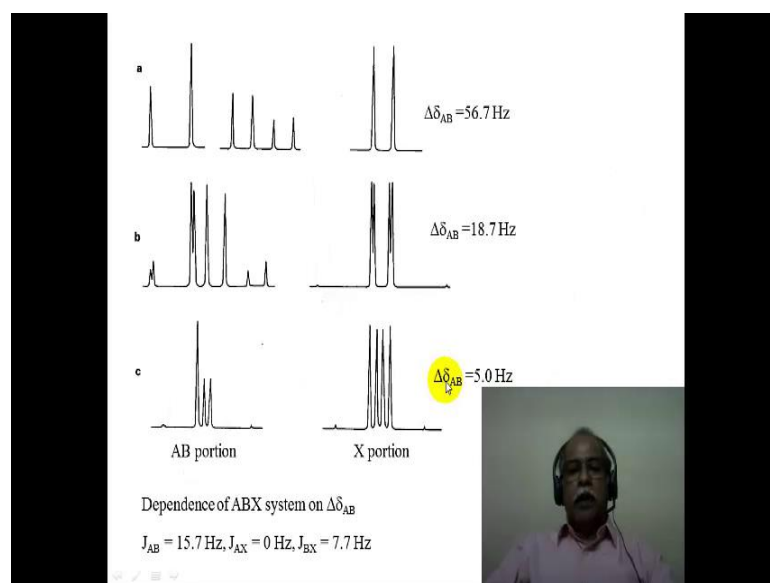
Now, these are the spectral pattern variation that one would observe, as you increase the delta delta from 5 hertz to 18.7 hertz to 56.7 hertz. In other words, the difference between the delta A and the delta B keeps increasing in this particular direction and that corresponds to the different kind of spectral pattern one can observe in the case of an ABX kind of a system.

Once again for clarity sake the AB part of this spectrum is shown on the left-hand side and the right-hand side shows the X part of the spectrum.

(Refer Slide Time: 21:19)

AB portion of the 60 MHz ^{1}H NMR spectrum of
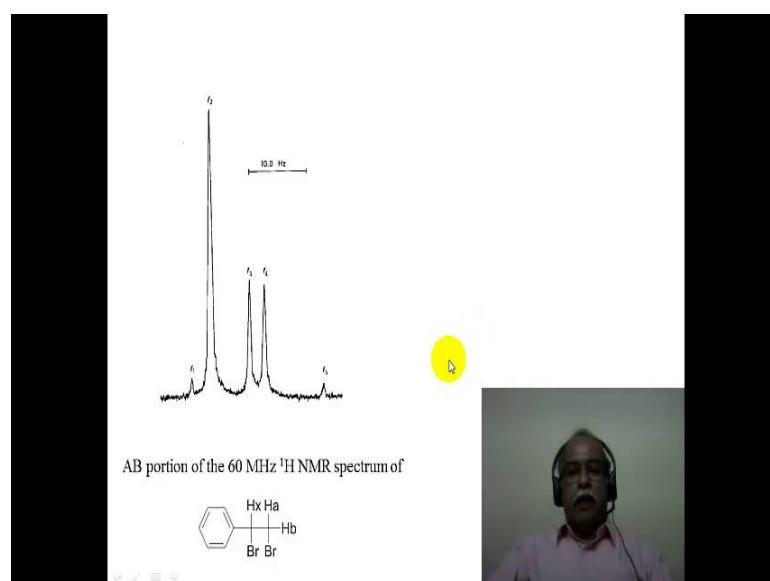
Here is a very unusual ABC kind of a spectrum or ABX kind of a spectrum as one can see here. And, this is rather difficult to interpret in terms of the line intensities and the number of lines that one sees in the ABX spectrum. This is truly a second order AB spectrum. ABX spectrum, because something looking similar to the classy or the bottom most spectrum of what is shown here is what this corresponds to, in terms of the AB portion of the; it is not even X portion is shown here only AB portion is shown here which corresponds to a pattern and similar to this one. This kind of a pattern, recognition is extremely important in order to interpret the spectral data for a second order spectrum.

(Refer Slide Time: 21:59)
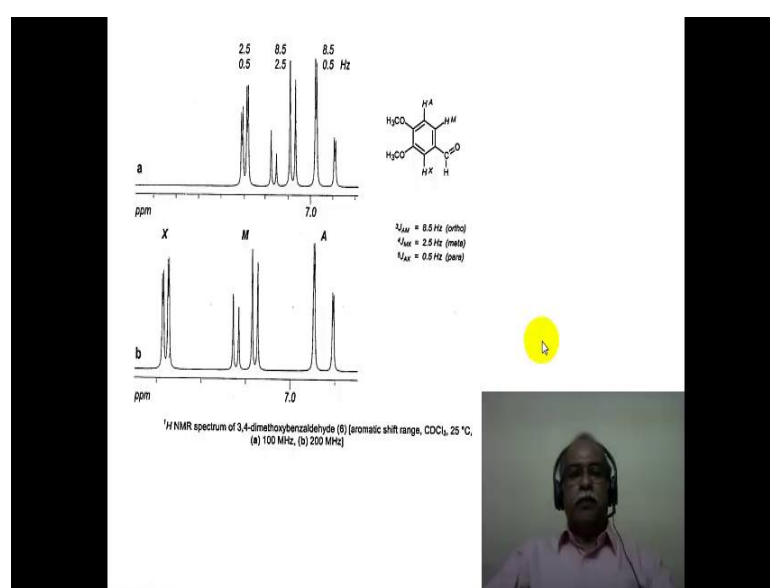
Analysis of the second order spectrum is fairly complex. One can simulate it by systematically varying the delta delta values and the J values until the calculated spectrum essentially matches with the experimental spectrum. Here is another example of a dimethoxybenzaldehyde derivative, which presents itself as an AMX spectrum. What is important here is the top spectrum and the bottom spectrum are recorded in 2 different frequency, the top spectrum is recorded in a 100 megahertz NMR spectrum a lower frequency and the bottom one is recorded in a higher frequency.

We will see the effect of spectrometer frequency in this spectrum very clearly. As you go from a lower spectrometer frequency to a higher spectrometer frequency, the spectrum tends to become a sort of a first order. Here you can very clearly see the X part to be a doublet of a doublet and the AB part which is further split into a doublet. In other words,

the 4-line pattern is further split into doublet of each line for example, because of the meta coupling with the meta coupling as well as the ortho coupling with the H m for example and H a for example or shown in this particular spectrum.

(Refer Slide Time: 23:13)


100 MHz ^{1}H NMR of (olefinic region)
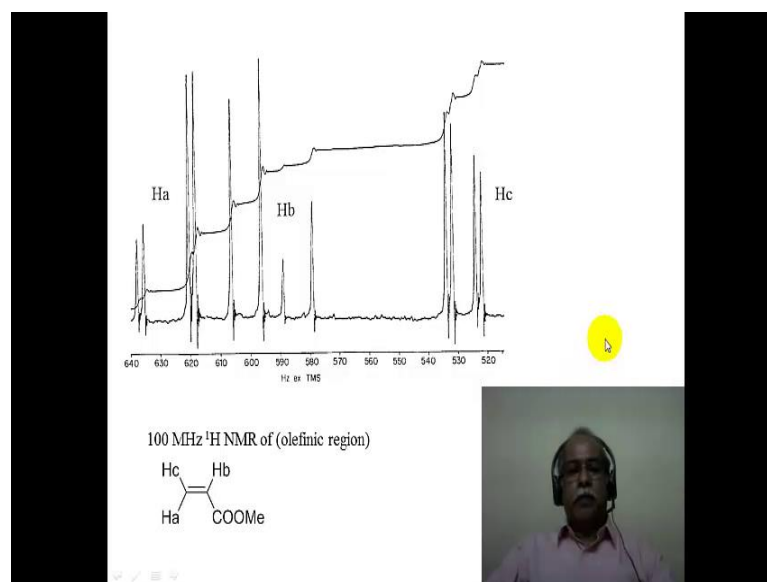
As I mentioned, a mono substituted olefinic derivative can present itself a fairly complex spectrum, the methyl acrylate is one such example. The X part of the spectrum is shown here which is labeled as Hc and the a b part of the spectrum is labeled here for example, which is Ha and Hb corresponding to the various spectrum. From this, one can easily extract certain information although delta values cannot be easily extracted, the J values can be relatively easy to extract from the spectrum. The gap between the small lines essentially correspond to the germinal coupling between the 2 hydrogen and the center of this particular doublet to the center of this doublet would essentially correspond to the H b c kind of a coupling, in other words the ortho coupling is what is seen here in this particular case.

Now, the gap between this 2 lines, that is starting from here if you call this line 1, line 2, line 3 and line 4; if you take the difference between line 1 and line 3 or line 2 and line 4 that was correspond to the trans coupling, which is this H a b kind of a coupling is what is seen here. The center of this lines and the center of these lines if we take and measure the coupling constant, that was correspond to the b c kind of a splitting pattern that you have here. One can also analyze this side, by taking a center of this doublet and center of

this doublet one can calculate the J a c. If we take the center of this doublet and center of this particular doublet here, and then measure the gap between these 2 centers that would correspond to J AB which is a trans (Refer Time: 24:53) of a coupling which is the largest coupling in this system.

(Refer Slide Time: 24:57)

100 MHz ^{1}H NMR spectrum (aromatic region) of
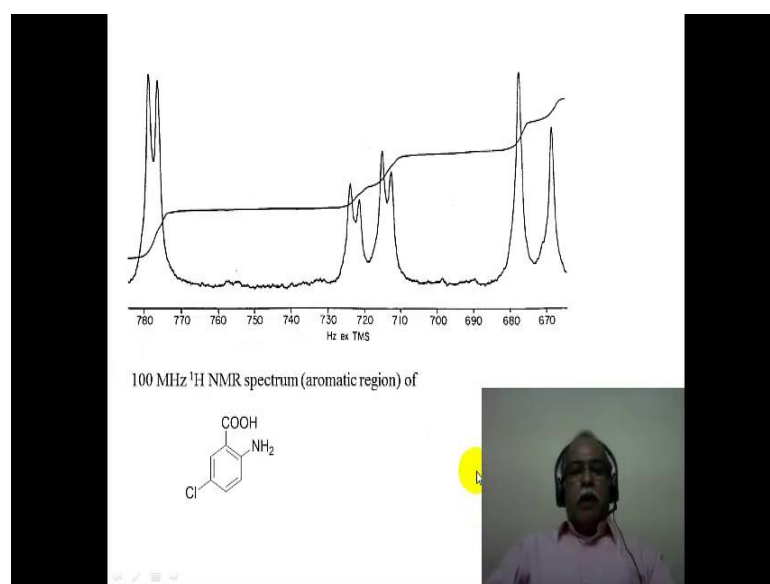
Here again a spectrum of chloro anthranilic acid is what is given. Now, this particular hydrogen which is adjacent to the chlorine and the COOH comes around 7.8 ppm, this is a 100 megahertz NMR spectrum, aromatic region alone is shown in this spectrum for example. And, the hydrogen that is ortho to the amino functional group would come as the lowest chemical shift value and that has an ortho coupling, so it is a doublet. Whereas, the hydrogen which is para to the carboxylic acid functional group has both ortho as well as the meta coupling, so, that comes as a doublet of a doublet.

This would also correspond to an AMX spectrum, except now, between A and X there is no coupling because the para coupling is either very small or negligible not seen in this spectrum.

60 MHz ^{1}H NMR spectrum of
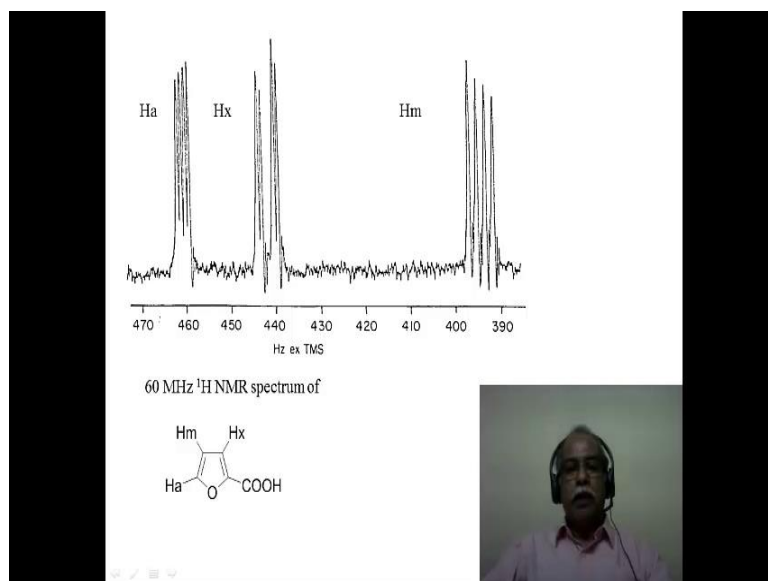
Here is a furan carboxylic acid derivative, 60 megahertz NMR spectrum, fairly easy spectrum to interpret because it is almost close to a first order spectrum. Although; it represents a Ha, Hx and Hm kind of a system in this particular instance. Each of this hydrogen is split by the other 2 hydrogen into a doublet of a doublet. So, the doublet of a doublet for each one of the hydrogen is essentially because of the mutual coupling between the A, M and X spin system and that is fairly easy to interpret in terms of getting the coupling constant value between the various hydrogen's in this particular spectrum.
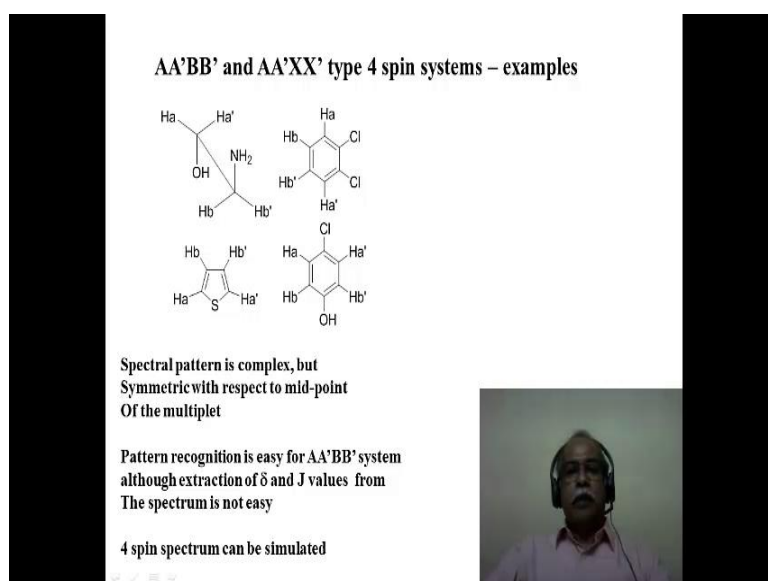
Now, let us come to the last part of the second order spectrum, namely AA prime BB prime or the AA prime XX prime kind of a system, which is a 4 spin system. Examples of AA prime BB prime or AA prime XX prime is given in this particular figure. If we consider disubstituted ethylene compounds, because of the fact that the average dihedral angel between the H a and H b, and H a and H b prime is not the same, geometrically the relationship between H a and H b, and H a and H b prime are different. So, mutually H a and H a prime, H b and H b prime, essentially represents chemically equivalent, but magnetically different spin system in terms of a and a prime, b and b prime for example.

An ortho disubstituted derivative, where the 2 substituents are identical constitutes AA prime BB prime system. A para disubstituted derivative, where the 2 substituents are different also constitutes AA prime BB prime system. In the case of thiophene furan and pyrrole for example, the ring hydrogens essentially represent an AA prime BB prime kind of a system. Now, the spectral pattern is fairly complex, but as mentioned earlier the spectral pattage is highly symmetrical with respect to the midpoint. So, one should be able to identify the multiplet by the symmetrical pattern that one sees. Pattern recognition is fairly easy for the AA prime BB prime system, we will see some examples.

(Refer Slide Time: 28:09)
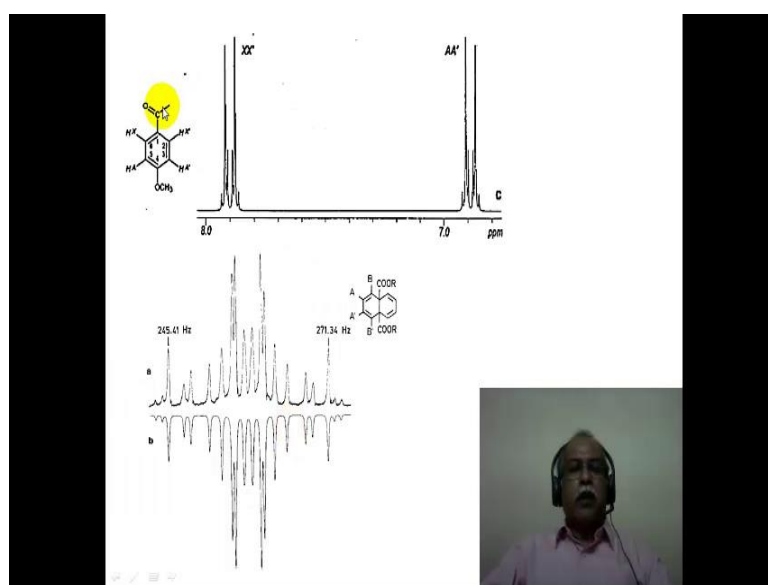
However, extraction of the various (Refer Time: 28:02) corresponding to the connectivity over here being the same on the other side also. So, it is a benzene

derivative which is a 4 4 prime dimethoxybenzyl and the ring hydrogen essentially constitute AA prime XX prime kind of a system. You can see here a doublet a major doublet for the X and a major doublet for the AA kind of a spin system essentially the coupling constant is the AX coupling constant which is the larger coupling constant that you see here.

In addition to that, you see a large number of fine lines at the bottom of the spectrum. So, this complex pattern essentially constitutes a second order spectrum of AA prime BB prime. There are 2 chemical shift values, namely delta A and delta X and several coupling constant value corresponding to J AX, AX prime AA prime so on. So, it is not easy to calculate the, extract the information regarding all the coupling constant the major coupling between A and X can be easily obtained from the spectrum because of the major lines essentially represent the coupling between the A and X in this case. It is another example; AA prime BB prime spectrum.

You can see how complex this spectrum is, except to appreciate the symmetrical nature of the spectrum from the center point, from the left-hand side to the right-hand side it is symmetrical. The top spectrum is actually the experimental spectrum, the bottom spectrum is a computer simulated spectrum by putting in the values for the delta values and the J values, until the values match the the spectrum that is calculated matches the exact spectrum that is obtained in the experimental part.

(Refer Slide Time: 29:56)

Dependence of AA'BB' spectrum on $\Delta\delta$

$(J = 8.2\,Hz, J' = 1.5\,Hz, J_a = 7.5\,Hz, J_b = 3.0\,Hz)$
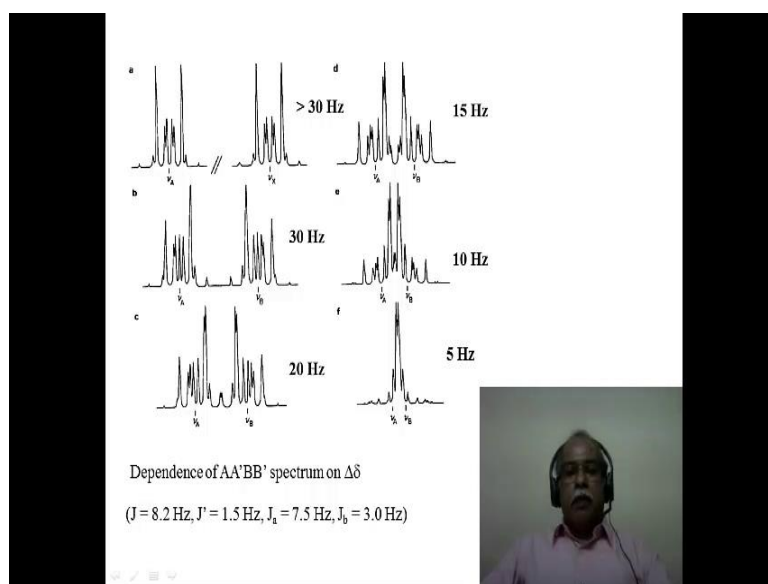
The AA prime BB prime pattern can quite drastically change depending on the delta delta value, keeping the J values constant. And, here are the spectral pattern, that one would anticipate for the AA prime BB prime pattern as you decrease the delta delta value from 30 hertz to about 5 hertz. Essentially, the delta delta divided by J ratio is systematically varied in this particular figure, showing the different kind of effect that the spectral pattern has with respect to the delta delta to the J value in the NMR spectra.

(Refer Slide Time: 30:32)
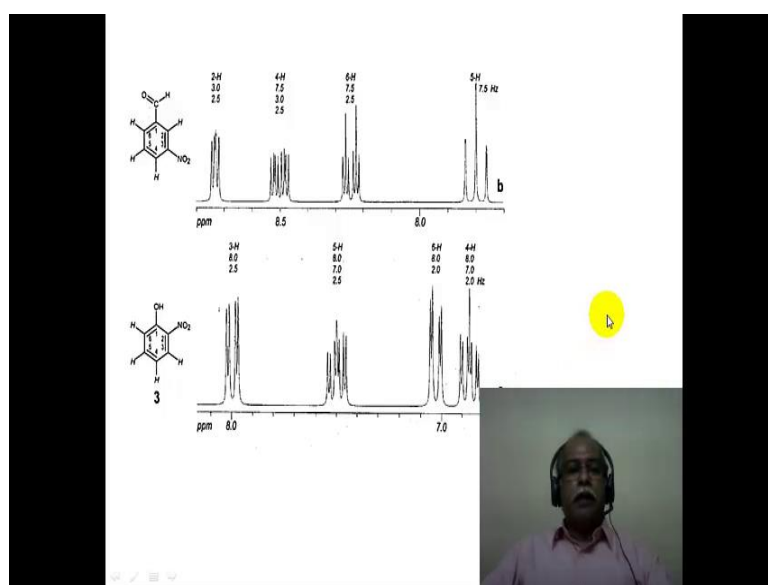
Here are 2 examples of spin system which are essentially a b c d kind of a system. These are fairly complex system, but since the spectrometer frequency is high in this cases. They can be fairly easily analyzed in these cases. Let us see if we can analyze this spectrum, this is meta nitro benzaldehyde; this spectrum of meta nitro benzaldehyde if you look at hydrogen number 5 which is this particular hydrogen, this is flanked by 2 ortho hydrogen, so one would expect a triplet for this if the 2 coupling constants are same. And, then if there is a para hydrogen which is not coupled then it would simply be a triplet.

In fact, the hydrogen number 5 which is labeled here is actually seen in more or less like a triplet, except that there is a small coupling between the hydrogen para to each other which is not very clearly seen in this case. So, only the ortho coupling is seen which is about 7.5 hertz, which is a gap between the line 1-2 or 2-3 can be taken this way. So, it is looking like more or less a first order spectrum only.

Now, if you take hydrogen number 6 which is this hydrogen. This has an ortho coupler, which is the ortho hydrogen which is coupled to it with a large coupling constant of about 7.5 hertz which is shown here. In addition to that, it also has 2 meta hydrogen, so the 2 meta hydrogen's if they couple with this particular hydrogen with identical J value then it would be a doublet of a triplet. Doublet because of the ortho coupling, triplet because of the 2 meta hydrogen. So, what you see is a doublet of a triplet, in other words 2 triplets is what you see and this is essentially analyzed as a first order spectrum.

Now, take the example of hydrogen number 4 which is in this position. This has an ortho hydrogen and the 2 meta hydrogens are not equally coupled. In other words, the meta coupling between these 2 hydrogen is different from the meta coupling between these 2 hydrogen. So, this would be a simple doublet of a doublet of a doublet, 8-line pattern is what one should see. One actually sees the 8-line pattern which is shown in this particular spectrum here.

Finally, if you look at the hydrogen which is flanked by the aldehyde under the nitro functional group, it has 2 meta hydrogen's, but the coupling constants are not identical. So, it would appear as a doublet of a doublet which is actually seen as a doublet of a doublet in this particular spectrum. In a similar manner, the ortho nitro phenol spectrum can also be analyzed, this is also a 4 spin system, such analysis is helpful in terms of identification of the compounds of the molecular structure.

So, what we have seen in this particular lecture is, the second order effect and the second order effect on a b type of a spectrum, the analysis of the a b kind of a spectrum in terms of extracting the delta values and the J values and the analysis of the AMX, AA prime BB prime kind of a spectra.

Thank you.