Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 30

Structure Solving based on IR, MS, 1H and 13C NMR Spectroscopic Data Problem Solving session – II

Hello, welcome to module 30 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. We will continue with the problem solving. This will be problem solving session two. We will use the information from infrared spectroscopy, mass spectrometry, proton and carbon 13 NMR spectroscopy for elucidation of structure of some simple organic molecule.

I always start with the interpretation of infrared spectrum, because it is my favorite spectroscopy. It is not necessary that one should start with infrared spectrum; one can always start with either proton NMR spectrum or mass spectrum or carbon 13 spectrum, which one – whichever one that you feel convenient, extract the information out of that particular spectroscopic data.

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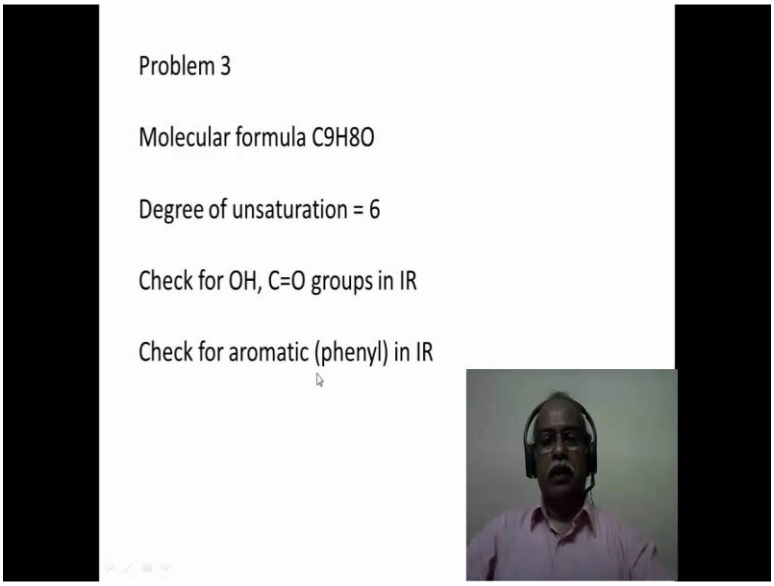

Problem 3

Molecular formula C_9H_8O

Degree of unsaturation = 6

Check for OH, C=O groups in IR

Check for aromatic (phenyl) in IR

This is problem number 3. Earlier in the other module, we saw the problem number 1 and 2. In problem number 3, the molecular formula is given as C9H8O. From the molecular formula, one can calculate the degree of unsaturation to be 6. So, one can assume that, this might be an aromatic compound, because a large degree of unsaturation; because remember that, phenyl ring has a degree of unsaturation of 4. Now, because of the presence of oxygen – because of the presence of oxygen in the molecular formula, we will carefully check the infrared spectrum for the presence or absence of OH stretching frequency, carbonyl stretching frequency. We can also check for the presence of any aromatic unit in the infrared spectrum.

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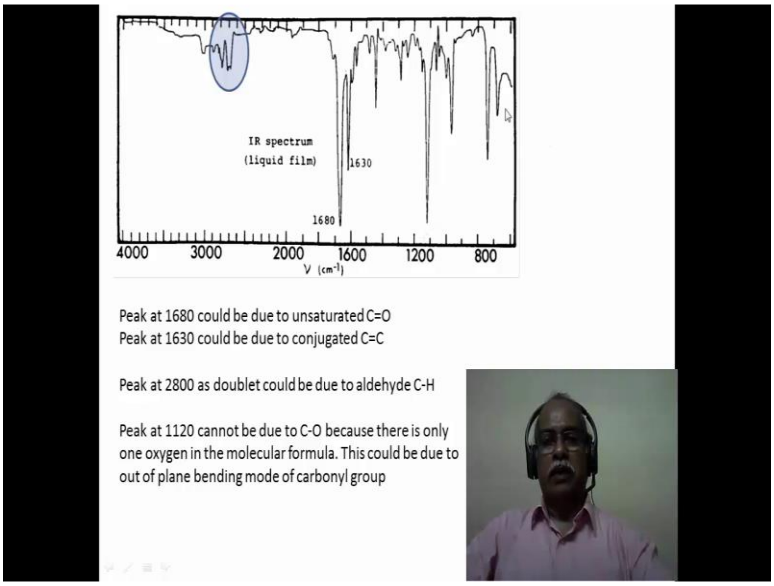

Peak at 1680 could be due to unsaturated C=O
Peak at 1630 could be due to conjugated C=C

Peak at 2800 as doublet could be due to aldehyde C-H

Peak at 1120 cannot be due to C-O because there is only one oxygen in the molecular formula. This could be due to out of plane bending mode of carbonyl group

This is the infrared spectrum of this particular compound. And a particular area is being highlighted in this particular spectrum and this is essentially because of the fact that this corresponds to the CH stretching frequency of aldehyde. It is a very characteristic region around 2800 or so and it appears always as a doublet. This corresponds to the CH aldehyde stretching. Now, there is a peak at 1608, which is probably due to alpha beta unsaturated carbonyl functional group; and, 1630 corresponds to C double bond C kind of a carbon – C double C kind of a stretching frequency. So, one can presume that, this molecule is an alpha-beta unsaturated carbonyl compound. The peak at 1120, which is fairly intense; it cannot be due to carbon and oxygen single bond stretching frequency because there is only one oxygen present and that is already accounted for a carbon double bond oxygen, because of the carbonyl stretching frequency that is very visible in the spectrum. So, this might be actually due to some kind of a carbonyl bending mode of the carbonyl group, which might be appearing around 1120 or so. So, let us not over emphasize the interpretation of this region, which is anyway a fingerprint region of that particular molecule.

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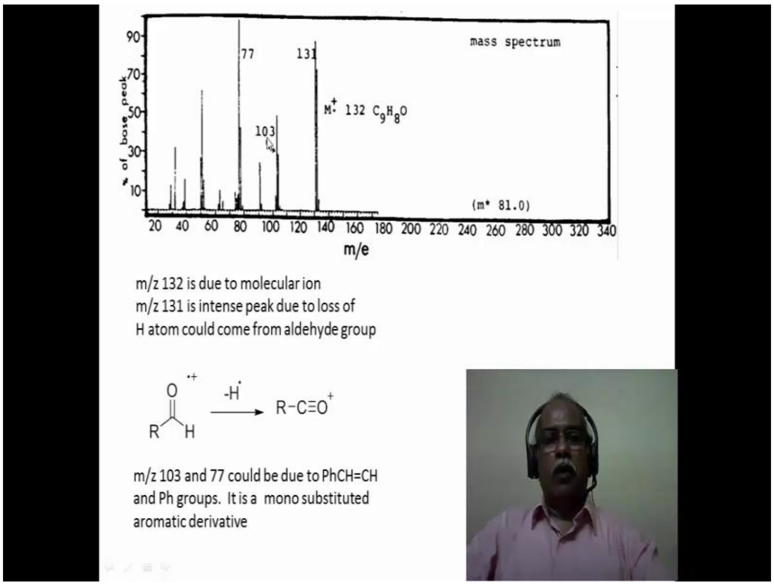

m/z 132 is due to molecular ion
m/z 131 is intense peak due to loss of
H atom could come from aldehyde group

m/z 103 and 77 could be due to PhCH=CH
and Ph groups. It is a mono substituted
aromatic derivative

Now, let us move on to mass spectrum. This is a mass spectrum of this compound. The molecular ion peak is seen at 132 m by z value. And, the molecular ion losses 1 mass unit to give 131, which is also a very intense peak. This is a very characteristic feature of an aldehyde carbonyl functional group. Aldehydes tend to react, tend to undergo the fragmentation by losing one hydrogen from the aldehydic site. This is represented here. So, if the aldehyde loses a hydrogen, it forms an acyl cation which is a resonance stabilized cation, so that fragmentation is usually very fusile in aldehydic compounds. You can also see that molecular ion decomposes or fragments to give 103 and 77 – 77 – 103 and 77 could be due to the phenyl CH double bond CH unit and 77 is because of the pheynl unit.

In other words, this is a mono substituted aromatic derivative. We can straight away tell from the fact that, the 103 is produced by the loss of carbon monoxide – loss of 28 mass unit corresponds to 103 and from 103, it is a loss of an acetylene unit corresponding to 26 mass unit, which gives a 77. So, from the molecular ion peak, you lose a hydrogen to give 131; then, lose a carbon monoxide to give 103 and lose an acetylene molecule to give 77. So, the fragmentation is fairly easy to understand in this particular case.

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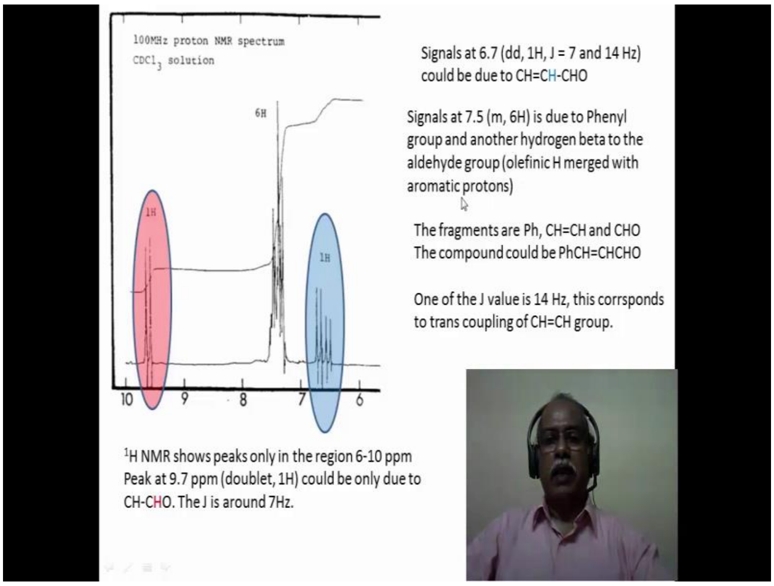

Signals at 6.7 (dd, 1H, J = 7 and 14 Hz) could be due to CH=CH-CHO

Signals at 7.5 (m, 6H) is due to Phenyl group and another hydrogen beta to the aldehyde group (olefinic H merged with aromatic protons)

The fragments are Ph, CH=CH and CHO
The compound could be PhCH=CHCHO

One of the J value is 14 Hz, this corrsponds to trans coupling of CH=CH group.

^{1}H NMR shows peaks only in the region 6-10 ppm
Peak at 9.7 ppm (doublet, 1H) could be only due to CH-CHO. The J is around 7Hz.

Now, this is the proton NMR spectrum of this particular compound. There are no peaks below 6 ppm delta value. That is why the region between 6 ppm and 10 ppm alone is projected in this particular slide. And, there is only one other peak, which is the TMS peak, which is in the 0 ppm region of the NMR spectrum. Now, the characteristic feature of this NMR spectrum is this region here around 9.7 or so; which is a very characteristic region for aldehydic hydrogen. So, we already know carbonyl group is present and aldehydic group – probably an aldehydic group is present from the infrared spectrum, that is, reaffirmed by the presence of this doublet in the NMR spectrum of this particular compound. It is a doublet because there is an adjacent vicinal hydrogen. If the red hydrogen – aldehydic hydrogen has an adjacent vicinal hydrogen, that would appear as a doublet.

Now, there is another multiplet here, which is a doublet of a doublet. This signal around

6.7 is doublet of a doublet with two coupling constants. The coupling constants can be easily measured. One can for example, take the resonance due to the aldehydic hydrogen and measure the coupling between these two lines. The frequency difference between these two lines will be 1 J value. And then, these two are mutually coupled to each other. One can also measure the same coupling constant between any adjacent peaks in this particular multiplet. If you take the center of the line 1 and 2 and center of line 1 and 3 – line 3 and 4, the center to center distance will be another coupling constant and that coupling constant turns out to be 14. If you want to do the measurement of the coupling constant, take a ruler; this is a 100 megahertz NMR spectrum. So, 1 ppm width is essentially 100 hertz. In other words, between 7 and 8 ppm, it is 100 hertz width. So, from that distance, if it is 100 hertz, one can always measure the gap between these lines as how many hertz in terms of the coupling constant of the system that we are dealing with.

We have now identified a fragment, which corresponds to CH double bond CH – CHO. This is CHO and this is the adjacent CH, which is the blue hydrogen, which is in the radiant shaded region. In other words, this blue hydrogen is split by the aldehydic hydrogen by 7 hertz. It is also split by another hydrogen, which is adjacent to this particular hydrogen by 14 hertz, because it is a very large coupling constant. The stereochemistry probably is a trans. In other words, a CH double bond CH in the trans coupling is what is responsible for the 14 hertz coupling.

Now, if this hydrogen is a beta hydrogen to the aldehyde, that would come very close to the aromatic multiplet. In fact, the aromatic signal if you see, this is 6 hydrogen intensity, it cannot be benzene because it is a mono substituted derivative. So, there is some other olefinic hydrogen, which is merging with this particular hydrogen and that is why the integration corresponds to 6 hydrogen. Totally, there are 6 plus 3 – 9 hydrogens in this molecule. The aldehydic hydrogen plus this particular hydrogen in this case and the 6 hydrogen – all these hydrogens are taken care of. This is – molecular formula is C9H8O. There are 8 hydrogen; one hydrogen the aldehyde, one hydrogen, which is a vinylic hydrogen; and, 6 hydrogen, which is a 5 hydrogen are of aromatic plus 1 hydrogen of the olefine merging on top of each other, which is the multiplet responsible for the signal around 7.5 or so. So, the signal at 7.5 is due to phenyl group and another beta hydrogen to the aldehyde. Olefinic hydrogen is merged with the aromatic proton in this case – particular case.

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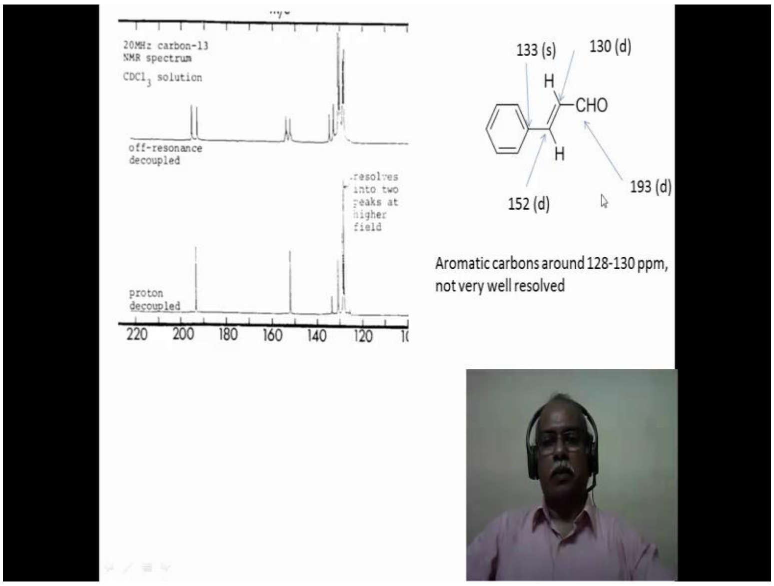

Aromatic carbons around 128-130 ppm, not very well resolved

If you look at the carbon 13 spectrum, carbon now from these fragments, one comes to the conclusion that, the molecule is probably cinnamaldehyde, which is phenyl CH double bond CHO. Let us confirm it by carbon 13 also. In the carbon 13 spectrum, the aldehyde comes at 193 ppm, which is a doublet in the off-resonance spectrum, because of the CH bond, which couples with the carbon; the hydrogen couples with the carbon to make it into a doublet.

Then, you have the alpha hydrogen and the beta hydrogen. Between alpha hydrogen and beta hydrogen, the beta hydrogen will come at a higher delta value. In other words, the peak around 152 corresponds to a doublet in the off resonance spectrum, which corresponds to the beta hydrogen. The alpha hydrogen comes around 130, which is again a doublet in this particular case. It is sort of merged with aromatic signal. And, this singlet which is around 133 for example, this peak here is essentially because of the ipso hydrogen. All the other aromatic carbons are essentially merged on top of each other. So, between 128 and 130, it is not a very well resolved spectrum to make assignments to the aromatic carbons of various type in this particular molecule.

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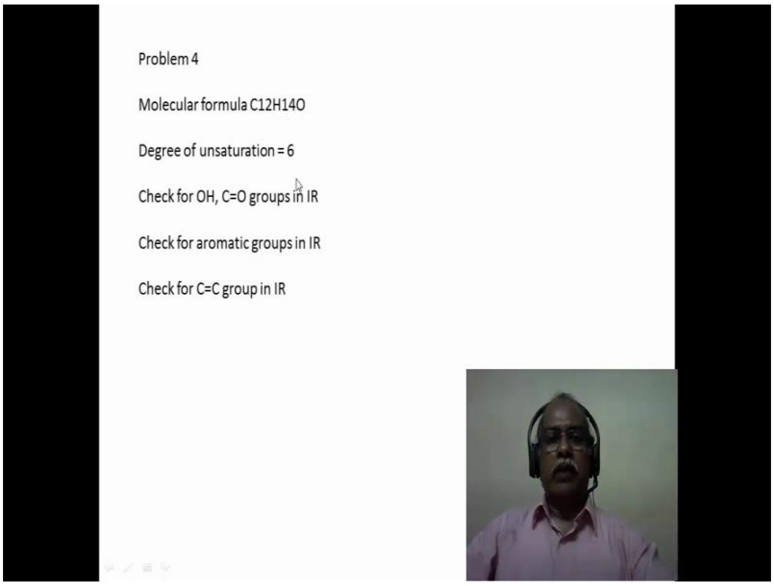

Problem 4

Molecular formula C12H14O

Degree of unsaturation = 6

Check for OH, C=O groups in IR

Check for aromatic groups in IR

Check for C=C group in IR

So, the molecule is readily recognized from the fact that, you have an aldehyde functional group both in the proton NMR spectrum, IR spectrum as well as mass spectrum; and, that it is an alpha beta unsaturated aldehyde from the splitting pattern that one sees, which leads to the conclusion that, it is a cinnamaldehyde in this particular instance.

Let us move on to problem number 4; problem number four, the molecular formula is given as C12H14O. The degree of unsaturation for this molecular formula is again 6. So, it could be again an aromatic compound. Because of the presence of oxygen, one should check for the OH functional group and carbonyl functional group whether it is present or absent; one can easily check in this particular case.

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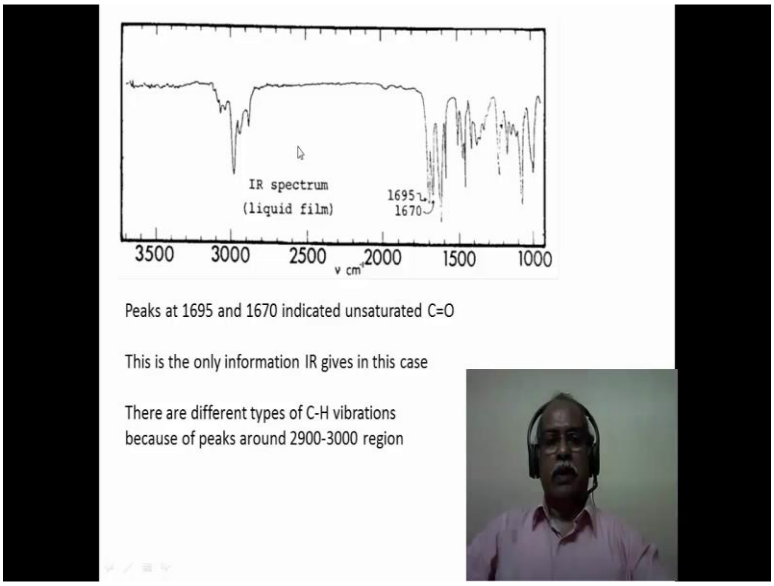

Peaks at 1695 and 1670 indicated unsaturated C=O

This is the only information IR gives in this case

There are different types of C-H vibrations because of peaks around 2900-3000 region

This is the infrared spectrum of this particular compound. The compound has a carbonyl stretching frequency at 1695 and 1670 in this particular case. These essentially indicate that you have an alpha-beta unsaturated carbonyl stretching frequency, because alpha-beta unsaturated carbonyl stretching frequency will be much lower than 1700. And, 1695 and 1670 fits the value corresponding to alpha beta unsaturated (Refer Time: 10:26) This is the only information that one can get from the infrared spectrum. One cannot interpret the fingerprint region and the CH region is of no use, because there will always be CH vibration in organic compounds. Most of the organic compounds will have CH vibration in this particular case.

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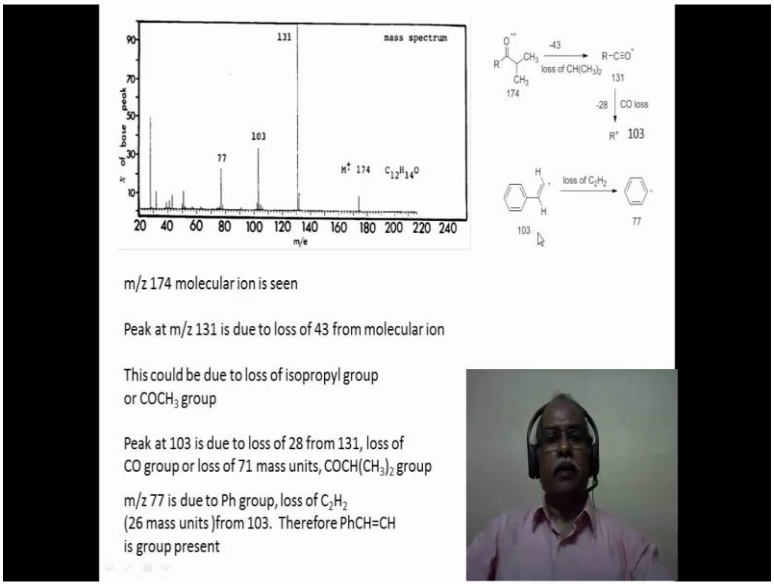

m/z 174 molecular ion is seen

Peak at m/z 131 is due to loss of 43 from molecular ion

This could be due to loss of isopropyl group
or $COCH_3$ group

Peak at 103 is due to loss of 28 from 131, loss of
CO group or loss of 71 mass units, $COCH(CH_3)_2$ group

m/z 77 is due to Ph group, loss of C_2H_2
(26 mass units)from 103. Therefore PhCH=CH
is group present

Now, let us have a look at the mass spectrum and see if we can interpret the mass spectrum. The molecular ion peak is seen at m by z value – 174 and 174 – the peak at 131 is due to the loss of 43 of the molecular ion. In other words, it should be losing either an isopropyl group or an acetylene group to go from 174 to 131. Now, the peak at 103 is again corresponding to the loss of 28 mass unit from 131 – 131 minus 28 correspond to 103; and, 70 – loss of 71 mass unit. In other words, this CO isopropyl group is responsible for the loss of 71 mass unit from 103 to 174. In other words, 174 minus 71 correspond to 103, which probably is due to the isopropyl carbonyl group in this particular case and the fragmentation pattern is represented schematically here. This is an isopropyl ketone. We conclude that, it is an isopropyl ketone mainly because of the loss of 71 mass units from 174 to 103.

In other words, a sequential loss of first an isopropyl group followed by a carbonyl group comes to – leads to the conclusion that, it is an isopropyl ketone kind of a system. Loss of propyl group minus 43 gives you the acyl cation. Loss of carbonyl functional group probably gives a stable cation, which is the 103 in this particular case. It is an aromatic compound, because the 103 leads to 77, which is a phenyl cation. In other words, loss of an acetylene unit from this particular molecule results in the formation of a phenyl cation, which corresponds to 77. So, we have essentially accounted for all the major fragmentation pattern in the particular system.

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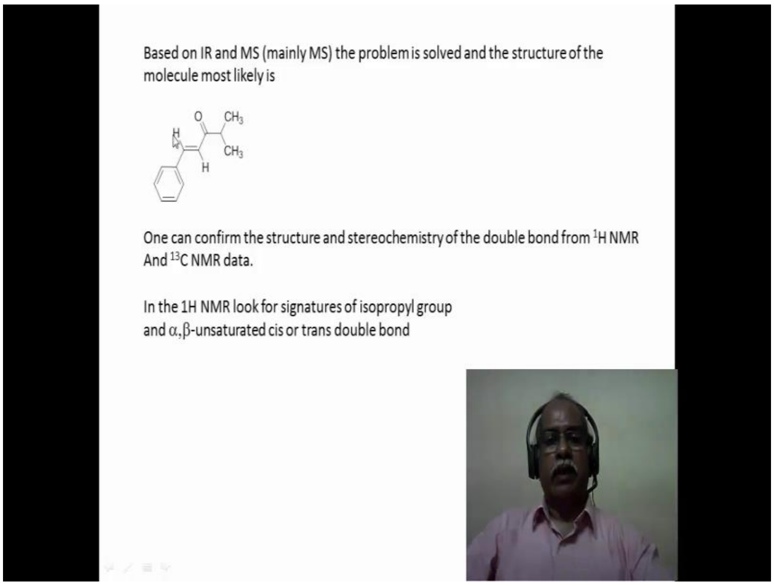

Based on IR and MS (mainly MS) the problem is solved and the structure of the molecule most likely is

One can confirm the structure and stereochemistry of the double bond from ^{1}H NMR And ^{13}C NMR data.

In the 1H NMR look for signatures of isopropyl group and α,β-unsaturated cis or trans double bond

So, the compound is easily identified as this particular system namely, isopropyl sterile ketone is the name of this compound. Based on the infrared and mass spectrum – mainly because of the mass spectrum, the problem is solved and the structure of the molecule most likely is this one. One can confirm from the proton NMR data as well as from the carbon 13 NMR data whether the actual molecular formula – molecular structure fit this data also. Since we have identified an isopropyl group, it should look for signatures of isopropyl group in the proton NMR spectrum; and, also look for an alpha beta unsaturated kind of a trans double bond or a cis double bond; one can look at the NMR spectrum.

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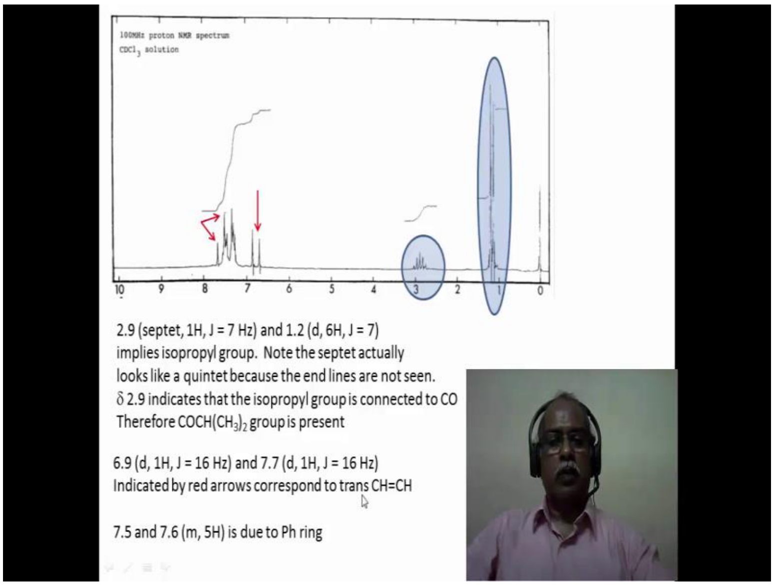

2.9 (septet, 1H, J = 7 Hz) and 1.2 (d, 6H, J = 7)
implies isopropyl group. Note the septet actually
looks like a quintet because the end lines are not seen.
δ 2.9 indicates that the isopropyl group is connected to CO
Therefore $COCH(CH_3)_2$ group is present

6.9 (d, 1H, J = 16 Hz) and 7.7 (d, 1H, J = 16 Hz)
Indicated by red arrows correspond to trans CH=CH

7.5 and 7.6 (m, 5H) is due to Ph ring

This is a proton NMR spectrum of this compound. One right away sees the signature of the isopropyl group. Please recall that, isopropyl group should give a septet and a doublet in terms of the CH and the CH3 splitting each other. But, the septet can be sometime deceiving. You see only 5 lines in this particular system. But, the integration tells you very clearly that, this corresponds to 1 hydrogen and this corresponds 6 hydrogen. If you measure the relative intensities of these two integration, this would be 1 is t o 6. So, this cannot be actually a quintet; it has to be a septet because CH – CH3 CH3 is what the fragment is we are referring to as isopropyl group. So, their end signal – in other words, the term – end lines are not seen very clearly in the case of the isopropyl group.

Then, come to the vinyl region. This is an aromatic region as well as the olefinic region. You have an alpha beta unsaturated aldehyde, which should give a doublet in the 6.8 region; another doublet which is indicated by the red arrows corresponding to the partner of this particular coupling partner. If you measure the coupling constant between these two lines; in other words, the frequency is 100 megahertz; so, between 6 and 7 ppm, it is 100 hertz. So, roughly, this would correspond to somewhere around 15 or 16 hertz, which corresponds to the trans CH double bond CH in this particular case.

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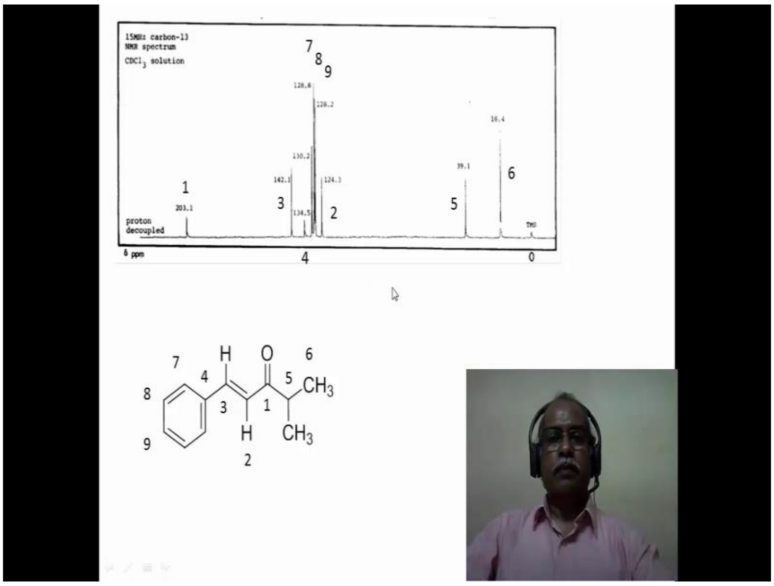

So, the molecule is isopropyl sterile ketone. One can assign the carbonyl stretching frequency at 203.1 which is an alpha beta unsaturated carbonyl corresponding to this one. Then, you have the beta hydrogen – beta carbon and the alpha carbon. The beta carbon should come at a higher delta value because of the resonance effect of the carbonyl functional group, which withdraws the electron and makes the beta carbon as depleted in electron density relative to the alpha carbon. So, one can see that very clearly. Number 3 corresponds to the beta carbon and number 2, which is at 124.3 corresponds to the alpha carbon in this particular molecule.

Then comes the CH carbon of the isopropyl, which is coming around 39.1 and the CH3 carbons of the isopropyl group, which is coming around 16.4 or so. The aromatic carbons are 7 and 8 carbons are essentially unresolved here. So, we do not know which one is which. But, we are sure that, this is because of the aromatic. There are three signals present here – 1, 2 and 3, which corresponds to the CH carbons of the aromatic unit. And finally, the lonely carbon, which is an ipso carbon here as a singlet with a less intensity is very clearly seen; which corresponds to the ipso carbon. The CH carbons have much higher intensity compared to the ipso carbon in this particular case.

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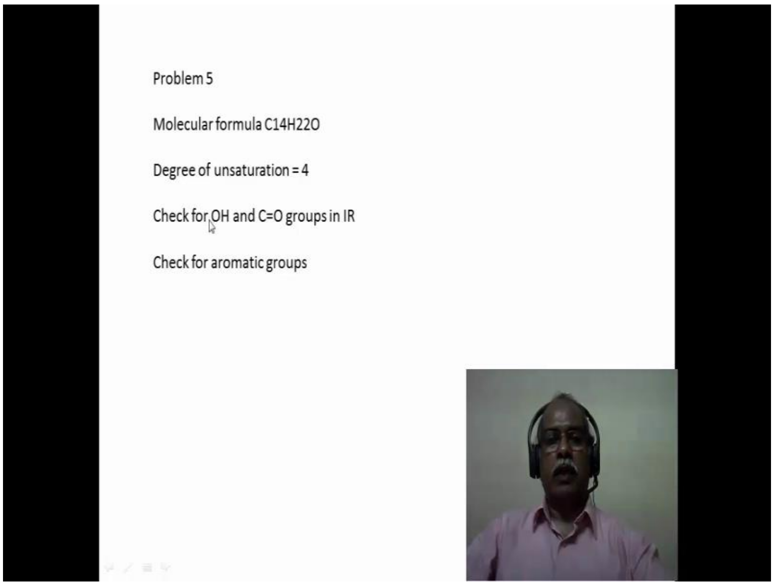

Problem 5

Molecular formula C14H22O

Degree of unsaturation = 4

Check for OH and C=O groups in IR

Check for aromatic groups

So, that is the isopropyl sterile case. Let us go on to another problem – problem number 5. The molecular formula is given as C14H22O. This molecule has a degree of unsaturation of 4. So, it could very well be an aromatic compound. Because of the presence of oxygen, once again let us check for the presence or absence of OH and the carbonyl stretching frequency in the infrared spectrum of this particular compound.

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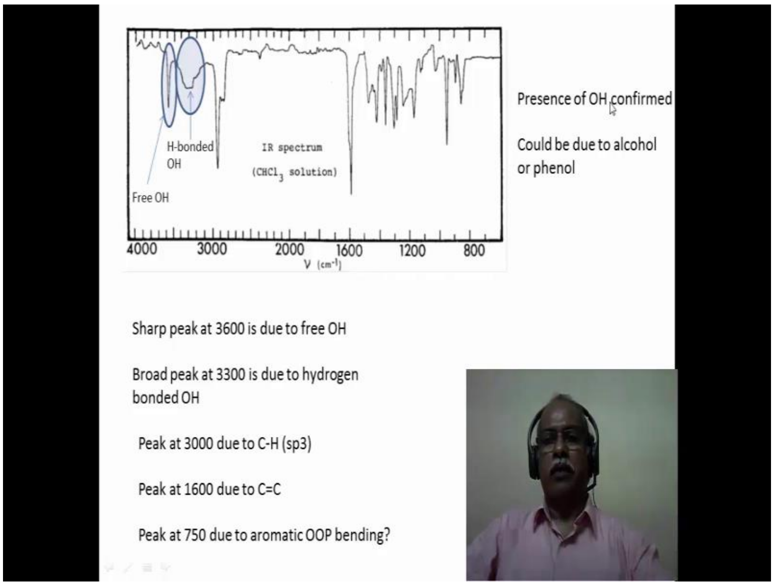

Presence of OH confirmed

Could be due to alcohol or phenol

Sharp peak at 3600 is due to free OH

Broad peak at 3300 is due to hydrogen bonded OH

Peak at 3000 due to C-H (sp3)

Peak at 1600 due to C=C

Peak at 750 due to aromatic OOP bending?

This is an infrared spectrum of the compound. This is fairly rich in information. You have a free OH, which is a sharp singlet kind of a peak is what is seen here. In addition to that, there is also a broad OH peak, which is a hydrogen bonded OH. This is a very characteristic feature of phenolic type of compounds, which undergo hydrogen bonding, but not completely. So, this is a solution phase measurement. Measurement is made in chloroform. So, depending upon the concentration, the intensity of the non-hydrogen bonded; in other words, the free OH and the hydrogen bond OH can be varying. I would presume that, this is a fairly dilute solution to be able to see the free OH in this particular compound. The sharp peak around 3600 is due to the free OH and another broad peak around 3300 is due to the hydrogen bonded OH in this particular system.

One can also see the 1600 peak, which is this particular peak, which may be due to the aromatic C double bond C stretching frequency and the peak around 750 or so – not 750, the peak around 850 or 900 is here. And, that corresponds to the out of plane bending type of a mode. And, this could be an out of plane blending type of a mode. We do not have to worry so much about this particular peak here. As long as we are able to see the OH peak as well as the C double bond C peak, we should be happy that we have got some information out of the spectrum of this kind. The presence of OH is confirmed; could be a phenol or an alcohol is the conclusion that we are arriving at.

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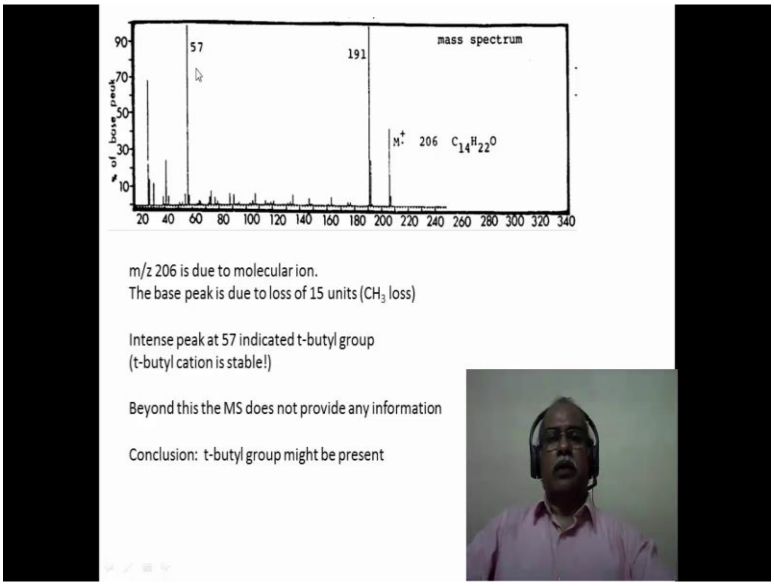

m/z 206 is due to molecular ion.
The base peak is due to loss of 15 units (CH_3 loss)

Intense peak at 57 indicated t-butyl group
(t-butyl cation is stable!)

Beyond this the MS does not provide any information

Conclusion: t-butyl group might be present

Now, the molecular ion peak is 206 m by z value – 206. The base peak is because of the loss of 15 mass units, which corresponds to the loss of a methyl group in this particular case. So, one 206 minus 15 corresponds to 191. And, another intense peak – 57 very clearly tells that, there might be tertiary butyl groups present in the system, because tertiary butyl group corresponds to 57. So, the molecule loses tertiary butyl groups to give a peak at 57, because tertiary butyl cation is a fairly stable cation.

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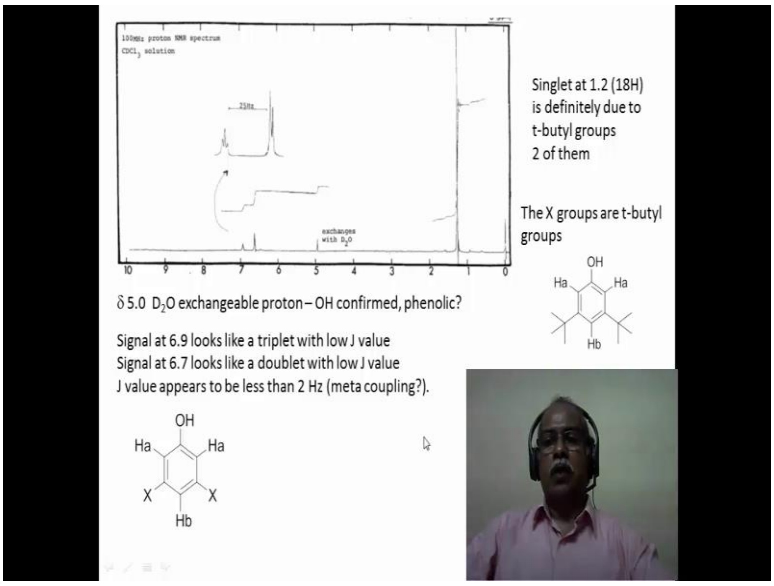

Singlet at 1.2 (18H)
is definitely due to
t-butyl groups
2 of them

The X groups are t-butyl groups

δ 5.0 D_2O exchangeable proton – OH confirmed, phenolic?

Signal at 6.9 looks like a triplet with low J value
Signal at 6.7 looks like a doublet with low J value
J value appears to be less than 2 Hz (meta coupling?).

The proton NMR spectrum is not a very informative spectrum in this particular case. This is an aromatic region. In the aromatic region, you see a triplet with a very small coupling constant. Before we go into that, let us see that, we have a OH, which is the a D2O exchangeable OH in this particular case. So, OH is come confirmed; it is most likely the phenylic OH that we are referring to. Signal at 6.9, which is this particular signal looks like a triplet with a very low coupling constant. j value is not easy to determine because it is much less than 2 hertz or so. One can tell from the experience that, this is not more than 1.5 or 2 hertz in terms of the coupling constant. We have a triplet and a doublet in this particular case. And so, the molecule must have some hydrogens a like this and the hydrogen b like this, which is meta substituted with reference to each other. So, these two – the integration corresponds to two hydrogen intensity here and one hydrogen intensity here, because the OH corresponds to one hydrogen intensity. And, compared to this one hydrogen intensity, this is a 18 hydrogen intensity, which is probably due to the presence of two tertiary butyl group in this particular case.

So, the 1.2 signal, which is this particular signal, is definitely due to the tertiary butyl group. Two of them are present because the 18 hydrogen intensity of a singlet can only be a tertiary butyl group in this case. So, the X groups are tertiary butyl groups in this particular instance. The reason we put the X groups meta to the OH is because we see the meta coupling between H a and H b, which is a very small coupling. If we consider H a, that will split H b into a triplet. So, this corresponding triplet is because of H b. And, the H b in turn will split the H a's into a doublet. So, c approximately a doublet in the region of 6.8 or so – 6.7 or so, in this NMR spectrum. So, this particular skeleton is consistent with the proton NMR spectrum. Although the proton NMR spectrum is not very well defined, the tertiary butyl group gives clue has to this kind of a molecular structure might be present in this. So, the compound is actually 35 di tertiary butyl; phenol is the compound.

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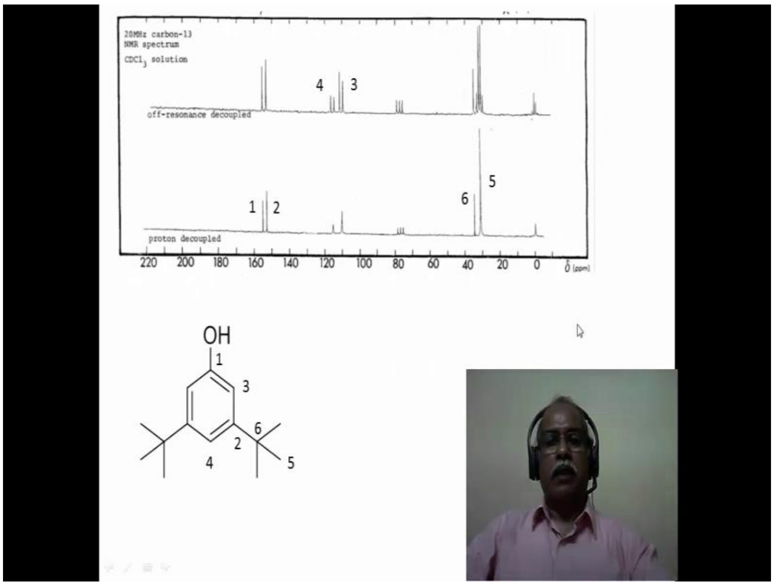

Let us see if the carbon 13 NMR also matches with this particular spectrum. The phenolic OH carbon will come in the region around 150 plus. So, this 155 peak, which is labeled as 1 corresponds to the ipso carbon. Then, comes the carbon number 2, which is the second ipso carbon bearing the tertiary butyl group. The molecule is half symmetrical; it has a symmetry plane. These two tertiary butyl groups are identical to each other. The tertiary butyl quaternary carbon 6 comes in this region as a singlet; and, the methyl carbons come as a quartet in the off-resonance spectrum, which is coming around 30 ppm or so in this particular case.

The aromatic carbons – the CH carbons of the aromatic system – carbon number 3 comes as a doublet and carbon number 4 also comes as a doublet. The one that is ortho to the OH will come at a lower delta value compared to the one para to the OH, which comes slightly at a higher delta value. So, the carbon 13 value for the CH carbons of this molecule correspond to 110 and 115 or so, because it is a phenolic compound and come much less than 120, which is justified. And, this triplet that you see here is because of the CD Cl 3 peak. This is a solvent peak is what is seen in the spectrum of this compound.

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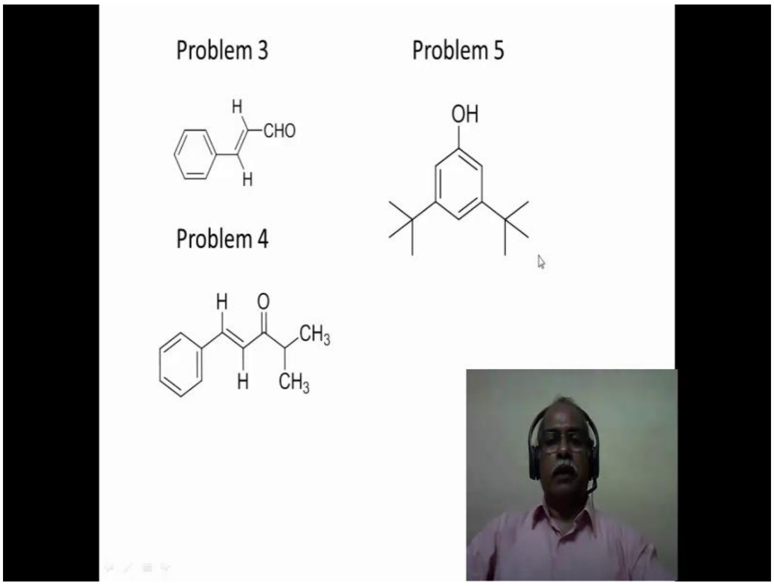
Problem 3

Problem 5

Problem 4

So, what we have seen in this module is three examples: two alpha beta unsaturated carbonyl compound; one is the aldehyde; the other is a ketonic compound. All of them are oxygen containing compound. Finally, we saw one compound, which is a phenolic compound heavily substituted with the tertiary butyl groups. So, the NMR gave way to identify the tertiary butyl group, because of the singlet intensity with 18 hydrogen could only be because of the tertiary butyl group. And, this is a kind of argument that we used for elucidation of the structure of these three organic molecules in this particular module.

Thank you very much for your attention.