Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 36
Structure solving based on IR, UV-Vis, MS, 1H and 13C NMR Problem solving session

Hello, welcome to the course on Application of Spectroscopic Methods in Molecular Structure Determination. This is module number 36. This will be the last module of this particular course, and this is considered to be a problem-solving session. We will look at the structure solving problems using infrared, UV-visible, mass spectrometry, proton and carbon 13 NMR spectroscopic data. At the end of this session, we will also give some tips, as to how to approach problem solving, problem solving sessions in the examination and so on.

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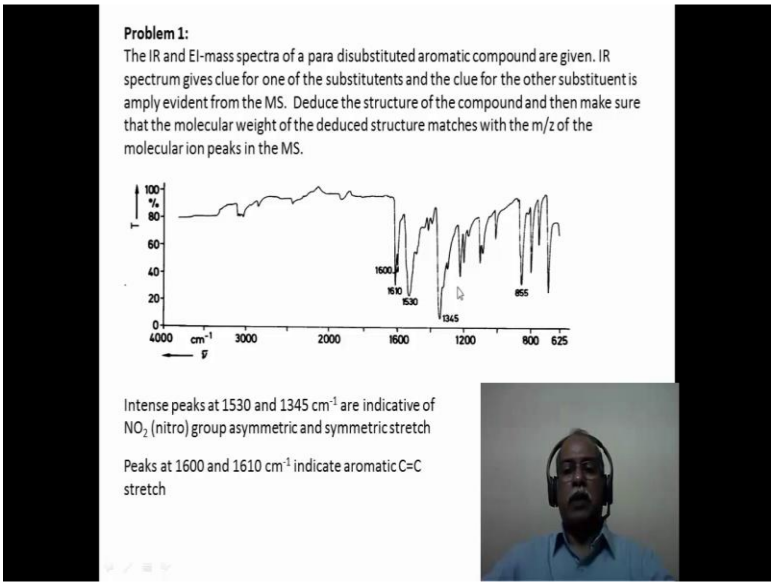

Problem 1:
The IR and EI-mass spectra of a para disubstituted aromatic compound are given. IR spectrum gives clue for one of the substitutents and the clue for the other substituent is amply evident from the MS. Deduce the structure of the compound and then make sure that the molecular weight of the deduced structure matches with the m/z of the molecular ion peaks in the MS.

Intense peaks at 1530 and 1345 cm^{-1} are indicative of NO_2 (nitro) group asymmetric and symmetric stretch

Peaks at 1600 and 1610 cm^{-1} indicate aromatic C=C stretch

Now, let us start with problem number 1. The infrared spectrum and the electrospray ionization spectrum of a para disubstituted aromatic compound are given. So, only two spectroscopic data are given. No other information is given. The infrared spectrum gives a clue for one of the substituents, and the clue for the other substituents is amply evident from the mass spectrum. Deduce the structure of the compound, and then make sure that, the molecular weight of the deduced structure matches with the m by z value of the molecular ion peak, seen in the mass spectrum. So, the compound is already shown to be the, given to be the para disubstituted aromatic derivative. So, all you need to do is, find out the 2 substituents from the two different spectroscopic data that is given, and see, whether it matches the mass spectrum, in terms of the molecular weight. This is a infrared spectrum of the compound.

From the infrared spectrum, very clearly seen that, there are 2 intense peaks, 1530 and 1345, one should immediately recognize this combination of peaks to be the nitro functional group in the infrared spectrum. The nitro functional group has an asymmetric, as well as the symmetric stretching of the NO bond. The asymmetric stretching comes at 1530, and the symmetric stretch comes at a lower frequency of 1345. And hence, one can confirm the presence of a nitro functional group, which is one of the substituents probably, in the para disubstituted derivative, from the infrared spectrum.

In addition to that, one can also see peaks around 1600, 1610, which is fairly obvious, because it is an aromatic system. The C double bond C stretch comes in this particular region. We do not know what is this peak due to? It maybe because of the other functional group. We will see whether we can find out, whether 855 corresponds to the other functional group. For the time being, let us not worry about the assignment of all the other peaks. We should be happy that, we have been able to identify the nitro functional group, from the infrared spectrum very clearly.

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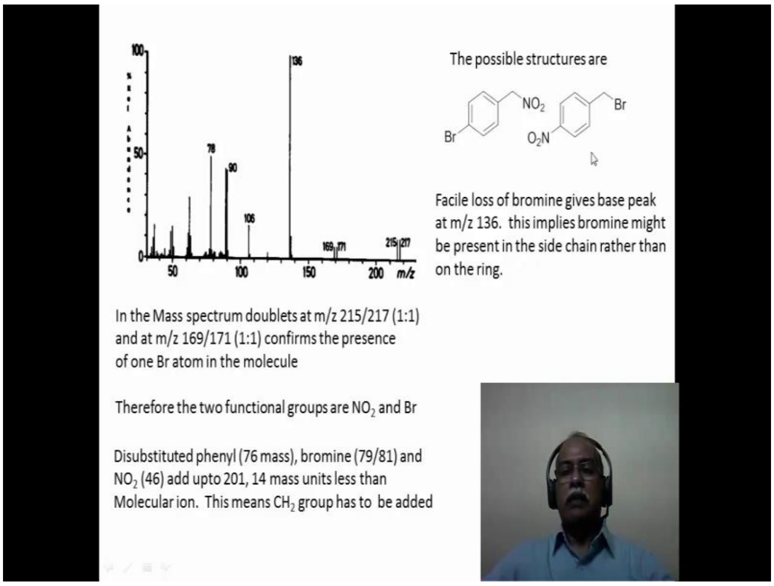

The possible structures are

Facile loss of bromine gives base peak at m/z 136. this implies bromine might be present in the side chain rather than on the ring.

In the Mass spectrum doublets at m/z 215/217 (1:1) and at m/z 169/171 (1:1) confirms the presence of one Br atom in the molecule

Therefore the two functional groups are NO_2 and Br

Disubstituted phenyl (76 mass), bromine (79/81) and NO_2 (46) add upto 201, 14 mass units less than Molecular ion. This means CH_2 group has to be added

This is the electron impact ionization mass spectrum of the compound. The striking free feature of this particular compound is that, the molecular ion peak; we have to assume that, this is the molecular ion peak. And, the molecular ion peak is a doublet of 2 mass unit difference, 215 and 217. The 215, 217, which is the 1 is to 1 intensity ratio, and the 169 and 171, which is also 1 is to 1 ratio, confirms the presence of a bromine atom in the molecule. So, the other substituent, actually, might be the bromine substituent. Therefore, the 2 functional groups, which are the NO 2 and the bromine are identified.

The NO 2 is identified from the infrared spectrum, and the bromine is unambiguously identified from the mass spectrum of this particular compound. So, if it is a diphenyl, disubstituted phenyl derivative, the molecular mass for the C 6 H 4 unit will be 76 mass unit. A bromine will be, 79, or 81, depending upon which isotope we are referring to; both are 1 is to 1 ratio. And, the NO 2 molecular weight is 46. If you add up the phenyl, bromine, and NO 2, which are the 3 functional group that we already know, it amounts to 201. The molecular weight is actually 215. That is 14 mass unit less than the molecular ion peak. This would mean that, the missing group could be a CH 2 functional group that may be present in the system.

So, based on this information, the 2 possible structures that can be written for this particular molecule, both are para disubstituted; both of them contain the Br, and the NO 2 group. In addition to that, we have added a methylene group. The methylene group is added between the nitro and the phenyl, in this particular case, and between the bromine and the phenyl, in the other case. So, we have to now identify, which one of these structure actually corresponds to the mass spectral data that is given here. There is a intense peak at 136, which is the base peak due to the loss of bromine atom.

Remember, whenever bromine is there, it would be a doublet of 2 mass unit difference, with the 1 is to 1 intensity ratio. If you subtract 79 from 215, you will essentially get 136. So, the loss of bromine gives a base peak at 136. This would imply that, the bromine is actually attached to the side chain, because, the benzyl bromide kind of a system readily undergo the rupture of the carbon-bromine bond, rather than an aromatic bromide, where the rupture of the carbon-bromine bond is much more difficult. So, most likely, the structure is para nitro benzyl bromide, for this particular compound.

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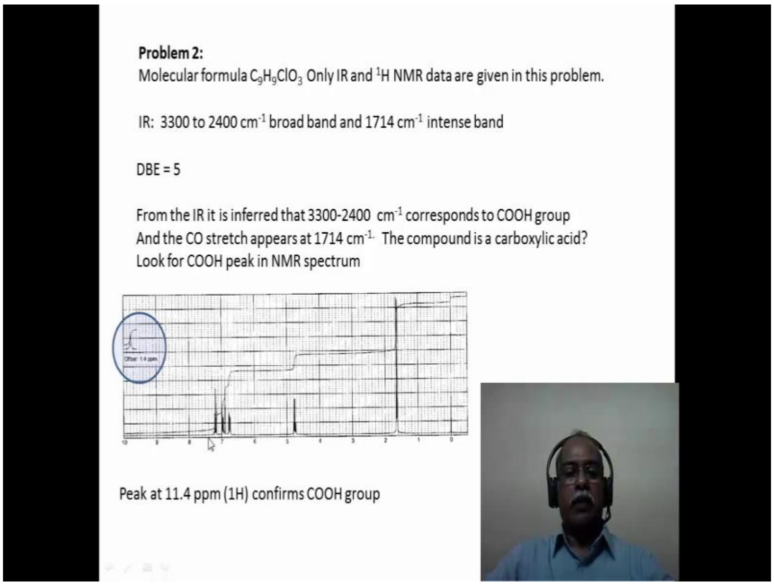

Problem 2:

Molecular formula $C_9H_9ClO_3$ Only IR and ^1H NMR data are given in this problem.

IR: 3300 to 2400 cm^{-1} broad band and 1714 cm^{-1} intense band

DBE = 5

From the IR it is inferred that 3300-2400 cm^{-1} corresponds to COOH group
And the CO stretch appears at 1714 cm^{-1}. The compound is a carboxylic acid?
Look for COOH peak in NMR spectrum

Peak at 11.4 ppm (1H) confirms COOH group

So, it is a fairly simple problem that we dealt with. Let us go to problem number 2. Molecular formula is given as C9H9ClO3, and the IR and the NMR spectra of this compound, is given in the problem. The infrared spectrum shows a broad peak between

3300 to 2400. This broad peak, of such a broad range, could only be because of a carboxylic acid functional group. In addition to that, there is a carbonyl peak also, which corresponds to a saturated carbonyl functional group, which could be a carboxylic acid functional group. The double bond equivalence is 5 for this molecule, calculated based on the molecular formula.

From the infrared spectrum, we come to the conclusion, there is a carboxylic acid functional group, and the CO stretch of the carboxylic acid functional group, essentially comes at 1714 inverse centimeter. If it is a carboxylic acid functional group compound, we should look at the NMR, and see, whether there are any acidic hydrogen in the molecule. This is the NMR spectrum of this particular compound. Sorry for the poor quality of the spectrum. These multiplet regions will be extend, expanded later, and shown very clearly.

For the time being, focus on the signal that is circled here, for example. It says, offset of 1.4 p p m; in other words, the spectrometer is scanned up to 10, and beyond that, whatever is scanned was offset, and plotted on the same scale here. So, the offset of 1.4 p p m essentially means, 10 plus 1.4 p p m, which will be 11.4 p p m, for this particular hydrogen. The integration of this hydrogen is 1 hydrogen. 11.4 p p m of 1 hydrogen intensity could essentially match the COOH functional group. Therefore, the presence of a COOH functional group is essentially confirmed from the NMR spectrum by the acidic hydrogen, which appears at 11.4 p p m, in this particular case. Now, this region, which is the aromatic region, between 6.9 to about 7.4 p p m or so, is expanded.

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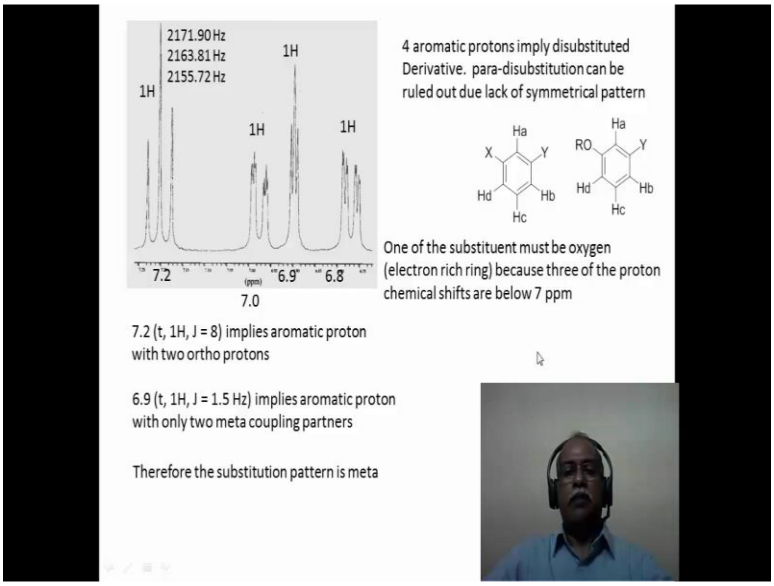

4 aromatic protons imply disubstituted Derivative. para-disubstitution can be ruled out due lack of symmetrical pattern

One of the substituent must be oxygen (electron rich ring) because three of the proton chemical shifts are below 7 ppm

7.2 (t, 1H, J = 8) implies aromatic proton with two ortho protons

6.9 (t, 1H, J = 1.5 Hz) implies aromatic proton with only two meta coupling partners

Therefore the substitution pattern is meta

The expansion is shown here very clearly. This is a triplet, and the 3 line pattern is, the frequency of the 3 line pattern is very clearly shown. This would correspond to, essentially 7.1, 7.1 p p m or so, in this particular case. There are 4 aromatic hydrogen in the molecule and 4 protons will be employed, as it is a disubstituted aromatic derivative. It is certainly not a para disubstituted derivative, because of lack of symmetry in the molecular pattern. If it is a para disubstituted derivative, it would be an AA prime BB prime pattern, which will have a symmetrical pattern in the NMR spectrum, which is not so. So, this is definitely not a para disubstituted derivative.

The 7.2 triplet, which is this signal, here, essentially implies, there are 2 ortho hydrogens to this particular, because, this is corresponding to an ortho coupling of about 7 hertz or so; that is what we have seen from the NMR spectrum of this. 8.1 hertz is the coupling constant that we are seeing, and that would essentially correspond to an ortho type of a coupling, in this particular case. This 6.9 p p m spectrum, this is a triplet, again. This triplet, and this triplet, is very different, because, this is a large coupling triplet, whereas, this is a very small coupling triplet. The coupling constant, in fact, is estimated to be about 1.5 hertz or so. This would correspond to 2 meta coupling partners, corresponding to this particular hydrogen.

In other words, this hydrogen has 2 meta hydrogen, and this particular proton has 2 ortho hydrogen. Such a substitution pattern is possible only with the substitution pattern of this type, where you have the H c, which has 2 ortho partner, coupling partners, and the H a, which has 2 meta coupling partners, for example. The H c d and the H c b, the couplings are equivalent, because they are ortho coupling. Similarly, between H a d and H a b would also be identical, to make this as a triplet. So, the H a is essentially, this particular hydrogen, here, and the H c is essentially, this hydrogen. H b would be a doublet of a doublet. It will be a doublet with the ortho coupling with H c; another doublet with the meta coupling with this H. So, one should see, a doublet of a doublet kind of a spectrum is what is seen in this NMR spectrum.

It is a fairly complex spectrum, because it has 2 multiplets; one corresponding to this meta coupling, and the other one corresponding to this meta coupling, the third one corresponding to the ortho coupling. In fact, it would be a doublet of a doublet of a doublet, and that is, the small coupling is not very clearly seen; only the ortho coupling is seen. So, one of these hydrogen corresponds to H b; the other hydrogen, which is here, corresponds to H d. So, one other information that we can get from the chemical shift value is that, if you have any signal below 7 p p m, that would only indicate that there is a strong electron donating group, making the aromatic ring as an electron rich ring, which would essentially shield the hydrogen.

If you look at this particular hydrogen, this is coming below 6.8; that would indicate that, this is directly attached to an oxygen kind of a heteroatom, which makes the ring as an electron rich ring. So, one can come to the conclusion that, one of the X group in the substituent is the O R group; let us identify, what is the R group, in this particular instance. The other multiplet that is seen here in the NMR spectrum is the multiplets which are in the region between 4.4 to 5 p p m. The other region, which is between 1 and 2 p p m, is the signal that we need to assign, and those multiplets are expanded nicely here.

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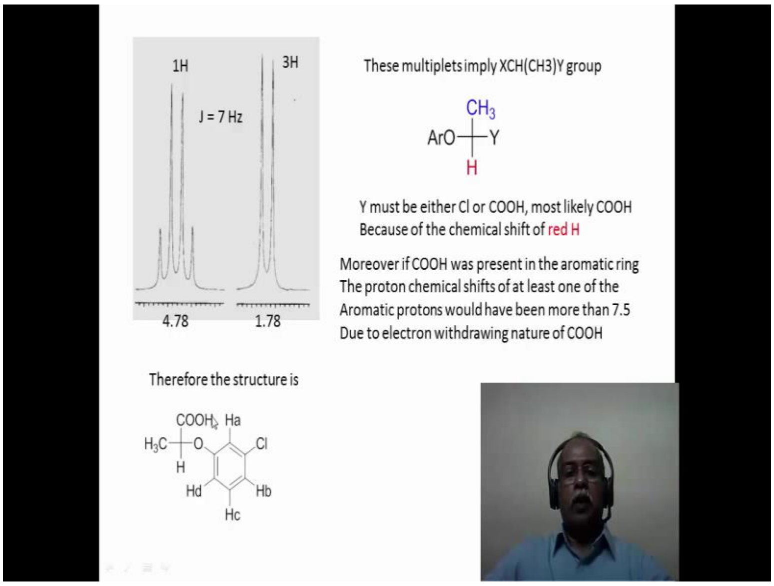

These multiplets imply XCH(CH3)Y group

Y must be either Cl or COOH, most likely COOH
Because of the chemical shift of red H

Moreover if COOH was present in the aromatic ring
The proton chemical shifts of at least one of the
Aromatic protons would have been more than 7.5
Due to electron withdrawing nature of COOH

Therefore the structure is

4.78 p p m is a quartet; 1.78 p p m is a doublet. A quartet and a doublet essentially would mean that, you have a CH 3 CH kind of a functional group. The red hydrogen would be a quartet, which is a 1 hydrogen intensity; and, the blue hydrogen will be a 3 hydrogen intensity of doublet. We have already identified an aryl oxy functional group from the earlier argument, that this is a aryl oxy functional group. So, we are looking at the R group in terms of the aliphatic signals that are seen in this particular instance. So, Y must be either a chlorine, or a carboxylic acid.

Most likely, it is a carboxylic acid, because of the chemical shift of the hydrogen red, which is X, which is the… Hydrogen red is essentially coming around 4.7 p p m. Normally, if it is directly attached to a oxygen bearing carbon, it will come around 4.1 p p m or so. If there is another electron withdrawing functional group, like the COOH is attached, then, it is likely to come at 4.78. Moreover, if the carboxy functional group is attached to the aromatic ring, that will essentially have one of the hydrogens at least deshielded, to coming around 7.5 p p m; but there are no signals around 7.5 p p m, we can see here; the signal stops around 7.25 or so, here. So, the carboxylic acid cannot be attached to the aromatic ring; it can only be attached to the side chain. So, the chlorine is attached to the aromatic ring, and the side chain is attached to, the carboxylic acid group is attached to the side chain, in this particular case. So, the molecule is actually, meta chlorophenoxy propionic acid is the molecule that we are referring to.

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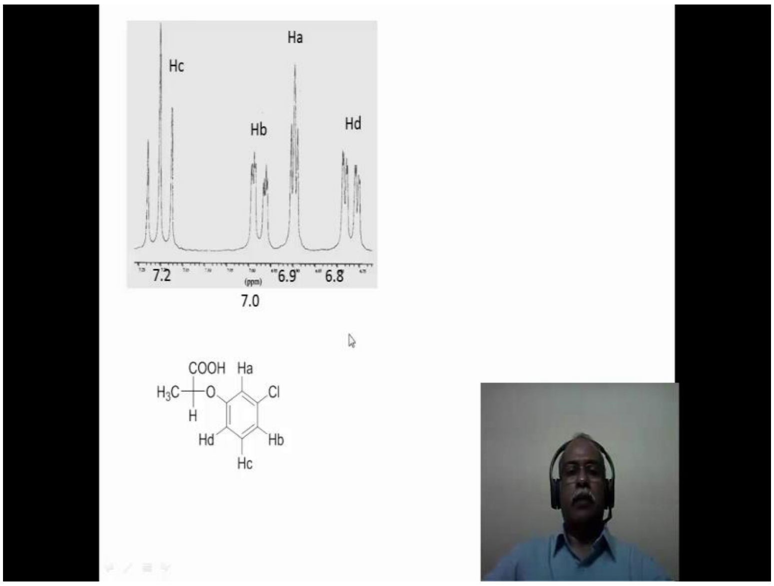

Let us see if we can assign the peaks also. H a, which should be a triplet because of b and d, essentially comes as a triplet with a meta coupling. The meta couplings are accidentally equal; that is why, it looks like a triplet, here. H c is also a triplet, because of the ortho coupling; accidentally, the 2 ortho coupling are same. So, it appears as a triplet, in this particular case. H b is fairly complex, which is coming in this region, here. H a is adjacent to the oxygen; that is why, ortho to oxygen comes at the lowest delta value. So, H d will have a ortho coupling, and two meta coupling partners, H a and H b. Maybe, the H a H d coupling is different from the H b H d coupling. So, it is fairly, multiplet kind of a thing is what is seen here.

I would say, this is a doublet, because of ortho coupling. Again, doublet, because of the meta coupling; one more doublet, because of the coupling with the partner b, for example. So, it will be a doublet of a doublet of a doublet; 8 line pattern is what is seen. But the meta couplings are so small that, you do not see it very clearly, in this particular case. Only the ortho coupling is seen as a large coupling. So, essentially, this satisfies the proton NMR spectrum of the compound. So, one has identified the structure of the compound, essentially from the fact that, you have an infrared spectrum, as well as the proton NMR spectrum. Only with these 2 spectral data, it was possible to identify the compound. The infrared spectrum gave clue for the functional group that is present, and the molecular formula gave the clue for the second substituent, which might be the chlorine substituent. The proton NMR spectrum gave the skeletal information. So, based on this information, we have arrived at the structure, which is this particular structure, which matches the given spectroscopic data. Now, the assignment is also very clearly seen; H a, H b, H c, H d are assigned very nicely. The multiplets can be easily explained, based on the fact, you have ortho and meta couplings, in this particular instance.

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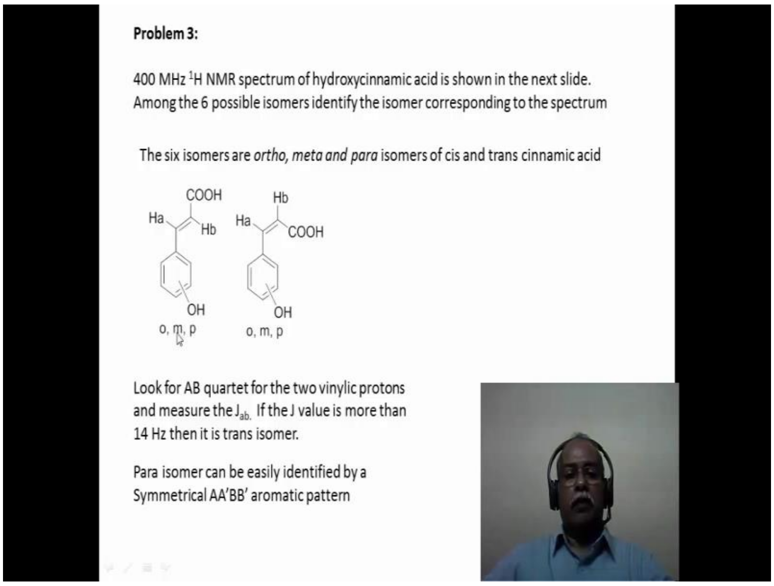

Problem 3:

400 MHz ^{1}H NMR spectrum of hydroxycinnamic acid is shown in the next slide. Among the 6 possible isomers identify the isomer corresponding to the spectrum

The six isomers are *ortho, meta and para* isomers of cis and trans cinnamic acid

Look for AB quartet for the two vinylic protons and measure the J_{ab}. If the J value is more than 14 Hz then it is trans isomer.

Para isomer can be easily identified by a Symmetrical AA'BB' aromatic pattern

Let us move on to the next problem. A 400 megahertz NMR spectrum of hydroxycinnamic acid is shown. Actually, the compound name is given as hydroxycinnamic acid. The problem is essentially to identify, of the 6 possible isomers, which one of the isomer, the spectrum correspond to, that is the problem. So, this is a fairly simple problem. 6 isomers are ortho, meta, and para of cis and trans; each cis, as well as trans, will have ortho, meta, para isomers. So, the three of the trans isomer, and three of the cis isomer, corresponding to ortho, meta, para hydroxycinnamic acid is what we are referring to, in this particular case.

Now, if it is a para isomer, we have to look for this 2 hydrogens, which are AB kind of a system; we have to look for the NMR spectrum, and see, whether we can measure the jJ value for the AB. If the AB is clean, seen very clearly, if the J value is more than 14 hertz, then you can assume that, it is a trans isomer. And, one can also see from the NMR spectrum, whether there is a symmetrical AA prime BB prime pattern present there. If it is present, then, it is definitely the para isomer; if it is absent, then, we can rule out the para isomer very clearly. So, the problem amounts to identifying the stereochemistry, to decide between cis and trans isomer, and identifying the aromatic pattern to decide on, whether it is a ortho, meta, para of a particular isomer.

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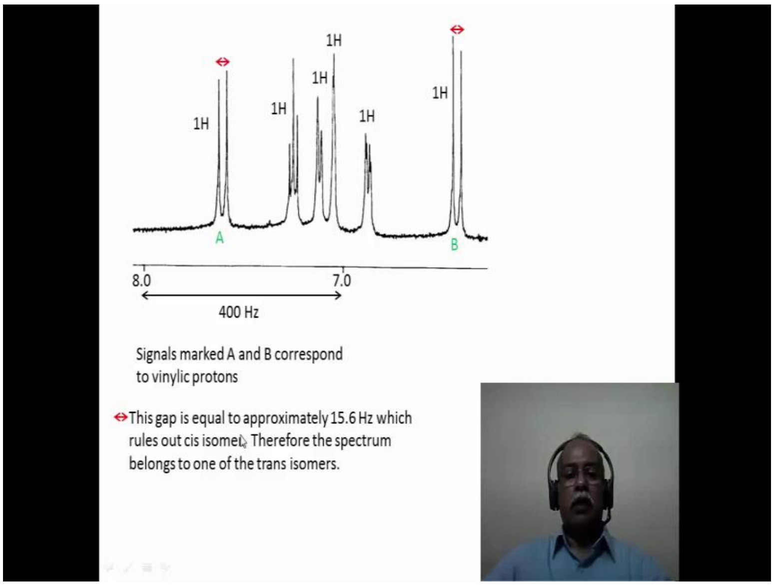

Signals marked A and B correspond to vinylic protons

⇔This gap is equal to approximately 15.6 Hz which rules out cis isomer. Therefore the spectrum belongs to one of the trans isomers.

So, this is the proton NMR spectrum. The two peaks, doublet are marked A and B, corresponds to the vinylic protons. This is the only AB quartet that you can see in this spectrum. So, this would correspond to A, which is close to the benzylic position, that is a beta hydrogen, and this is corresponding to the alpha hydrogen. This is a 400 megahertz NMR spectrum. The data is given as 400 megahertz. So, 1 p p m essentially corresponds to 400 hertz, in terms of the, width of this particular 1 p p m would correspond to 400 hertz. So, we need to calculate the width of these 2 lines, or the width of the 2 lines, as indicated by the red double headed arrow. You can either measure the coupling constant here, or measure the coupling constant here. I have done so. It corresponds to about 15.6 hertz. In other words, if this length is 400, what is this length corresponding to, that is all we need to find out. And, it turns out to be 15.5 hertz, and this is definitely, it belongs to the trans isomer.

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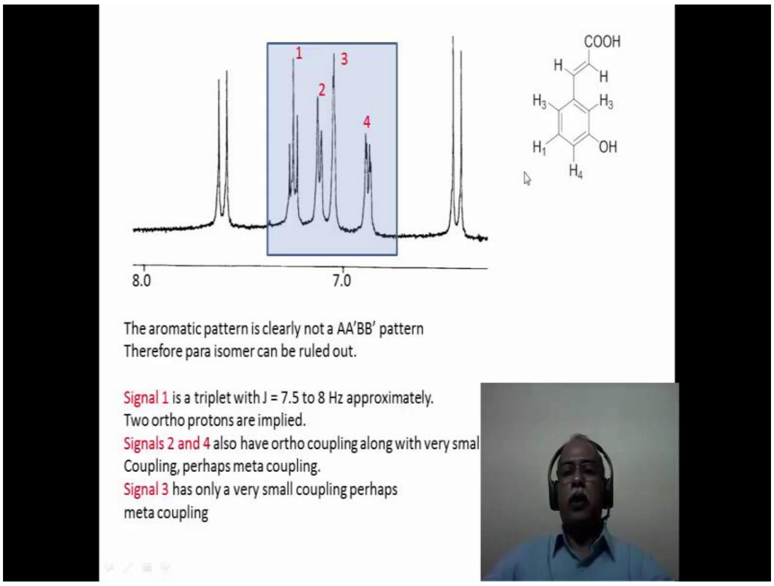

The aromatic pattern is clearly not a AA'BB' pattern
Therefore para isomer can be ruled out.

Signal 1 is a triplet with J = 7.5 to 8 Hz approximately.
Two ortho protons are implied.
Signals 2 and 4 also have ortho coupling along with very smal
Coupling, perhaps meta coupling.
Signal 3 has only a very small coupling perhaps
meta coupling

So, we will move to the rest of the aromatic hydrogens, here. The rest of the aromatic hydrogen, one can very clearly see a signal number 1, for example, is a triplet at 7.5 hertz to 8 hertz approximately, which would correspond to 2 ortho coupled products. In other words, this proton, aromatic proton, has two ortho coupled partners.

So, it appears as a triplet, for example. And, signal number 2 and 4 are essentially having an ortho coupling, and a very small coupling, which might be meta coupling; you can see, barely see the coupling. The coupling is ortho here. And, within the line here, there is a small coupling, which is a meta coupling, probably. Signal number 3 is essentially a singlet; it may be, a small doublet maybe present here, because of a very small meta coupling kind of a system.

So, based on this information, we can arrive at the fact that, this has to be a ortho hydroxy, or a meta hydroxy kind of a system; definitely not a para hydroxy kind of a system. One can rule out the structure also essentially, because, this hydrogen, which has

2 adjacent ortho hydrogen, would be a triplet, and this hydrogen which also has 2 adjacent ortho hydrogens would be a triplet; but, you see only one triplet in the spectrum. So, these 2 hydrogens, which would have been 2 triplets in this spectrum, the spectrum does not have 2 triplets. So, this can be easily ruled out as a structure. So, the structure has to be the meta hydroxy cinnamic acid. Now, we can assign, for example, the H 1, H 2, H 3, H 4 very easily.

Sorry, this is H 2, and this is H 3. I have mislabeled it. This is supposed to be H 2; H 1, H 2, H 3, H 4 is the signals that we see, for the corresponding. So, one can interpret H 1 to be a triplet, because of coupling to H 3 and H 2, H 4 and H 2; and, this would be, essentially, a singlet, which is H 3, for example. This would be an ortho coupling partner, and a meta coupling partner. So, most likely, it is the H 2 here, which is this H 2 here. H 3 will be a, again, a 2 meta coupling partner, and 1, no ortho coupling partner is there. So, essentially, H 3 will be a, essentially a singlet, in this kind of a system.

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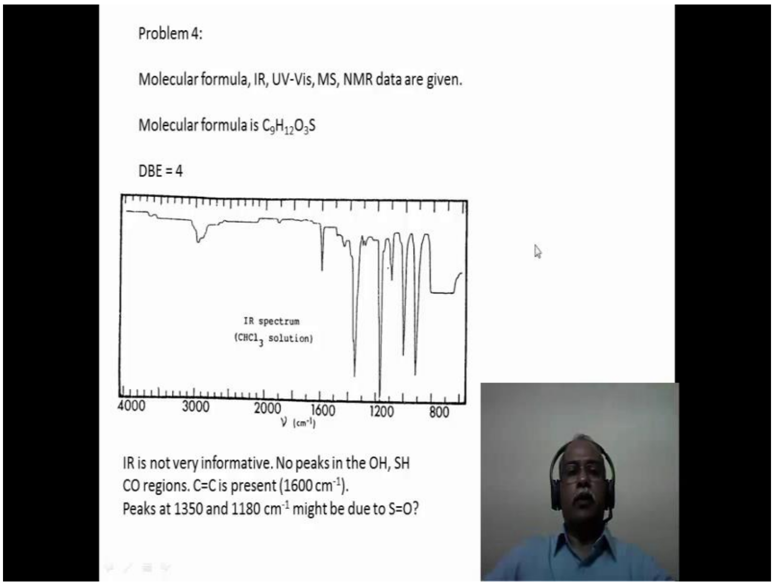
Problem 4:

Molecular formula, IR, UV-Vis, MS, NMR data are given.

Molecular formula is $C_9H_{12}O_3S$

DBE = 4

IR is not very informative. No peaks in the OH, SH CO regions. C=C is present (1600 cm^{-1}). Peaks at 1350 and 1180 cm^{-1} might be due to S=O?

Let us move on to the next problem. This is problem number 4. This is, molecular formula is given, and the infrared, UV visible spectrum, mass spectrum and NMR data is also given. This is the infrared spectrum of this compound. There are no peaks that are corresponding to the OH, NH, SH region, or the carbonyl regions. So, the infrared spectrum is not very informative, in this particular case. However, we can conclude that, there may be an unsaturation in the system, which corresponds to, 1600 peak at C double bond C stretching frequency is there. All the other peaks are coming in the fingerprint region. One can, for example, assume that, the peak around 1350, which is this particular peak, and the peak around 1180, which is this particular peak, maybe because of a sulphur oxygen stretching frequency; because sulphur is present in the compound, we are assuming this. If it is a SO 2 kind of a group, this could be an asymmetric stretch frequency of the SO, and this could be a symmetric stretch frequency of the SO; but, that is a very tentative assignment. But, we are not sure about this particular assignment. We need another confirmation, to make sure that this assignment is correct.

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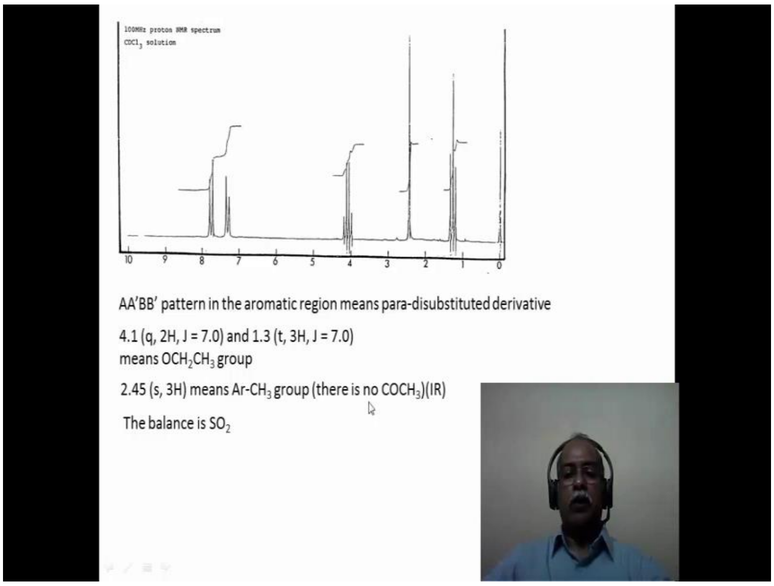

AA'BB' pattern in the aromatic region means para-disubstituted derivative

4.1 (q, 2H, J = 7.0) and 1.3 (t, 3H, J = 7.0)
means OCH_2CH_3 group

2.45 (s, 3H) means Ar-CH_3 group (there is no $COCH_3$)(IR)

The balance is SO_2

Proton NMR spectrum is very nice. You have a AB quartet, AA prime BB prime kind of a pattern, which immediately tells you that, in the aromatic region, you have a para disubstituted derivative kind of a thing. And then, 4.1, a quartet of 2 hydrogen intensity, 7 hertz coupling, and a triplet of 1.3 p p m of 7 hertz coupling; these are the coupling partners. So, this would essentially amount to, OCH 2 CH 3; OCH 2 because, this is about 4.1. The large chemical shift value tells you that, it has to be attached to an oxygen, and nothing else, that would come in the 4 region of the, in NMR spectrum. The 2.45 is a singlet. This would mean that, it is attached to an aromatic functional group. It could have been an acetyl type of functional group, but there are no carbonyl peaks in the infrared spectrum.

So, this can be easily ruled out. In the absence of the infrared spectrum, you cannot rule this out; but in the presence of infrared spectrum, which shows clearly, there is no carbonyl functional group, this can be ruled out very easily. So, this is a aryl CH 3 kind of a group. So, if you take the aryl CH 3, which is a para substituted aryl CH 3 and OCH 2 Ch 3, and subtract it from the molecular formula, the balance will be SO 2.

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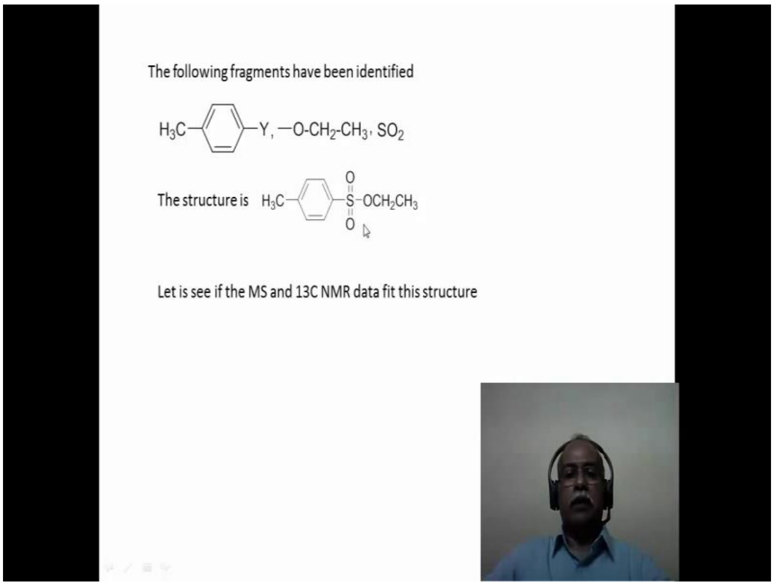

The following fragments have been identified

H_3C–C₆H₄–Y, —O-CH_2-CH_3, SO_2

The structure is H_3C–C₆H₄–$S(=O)_2$–OCH_2CH_3

Let is see if the MS and 13C NMR data fit this structure

So, we have identified the fragments, that it is a para tolyl y substituted derivative, and it is a, ethoxy functional group is there, and SO 2 functional group is there. You need to put them together; you arrive at the structure, that it is a para tolyl benzene sulphonic acid ethyl ester; in other words, ethyl para toluene benzene sulfonate is the structure of the compound. Now, we have to ascertain, whether the mass spectra and the carbon 13's data, also fit this particular structure.

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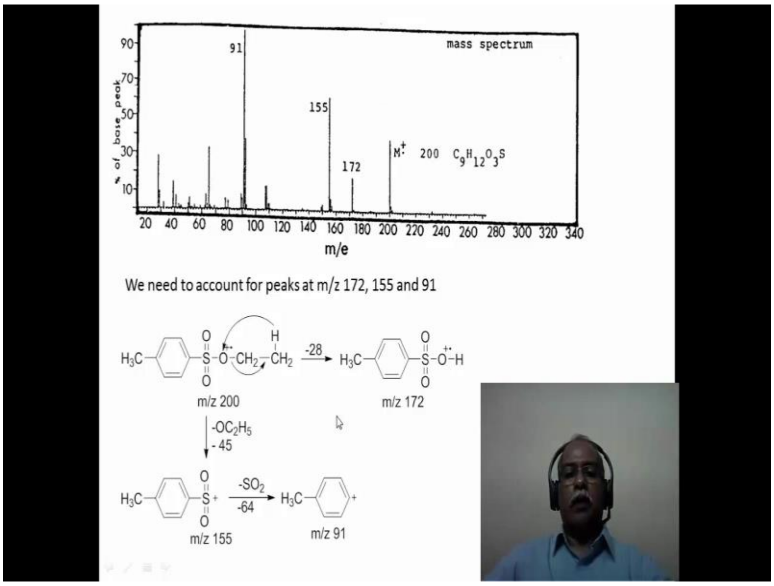

We need to account for peaks at m/z 172, 155 and 91

This is a mass spectrum of the compound. The molecular ion peak is very clearly seen at 200. Loss of 28 mass unit corresponds to 172, and loss of 45 mass unit corresponds to 155; and from here, loss of 64 mass unit corresponds to 91. So, let us see, if these particular peaks, these peaks can be identified by this fragmentation pattern. This is para methyl benzene sulphonic acid ethyl ester. This is a carbonium ion that is formed, a carbo cation that is formed in the mass spectral condition; a beta hydrate shift would essentially release the ethylene unit, which is a 25, 28 mass unit loss from the molecular ion peak.

If we subtract 28, we get 172; there is a peak at 172. And, a simple fragmentation corresponding to the sulphur-oxygen bond here, with the loss of ethoxy functional group, which is the loss of 45, would essentially correspond to molecular ion losing a ethoxy radical, to give 155 peak, which is this particular peak. Loss of sulphur dioxide from this molecule, will essentially give you the para tolyl cation, which is the 91 peak. So, all the mass spectral data can be satisfactorily explained by a simple fragmentation pattern of this kind, for this particular molecule.

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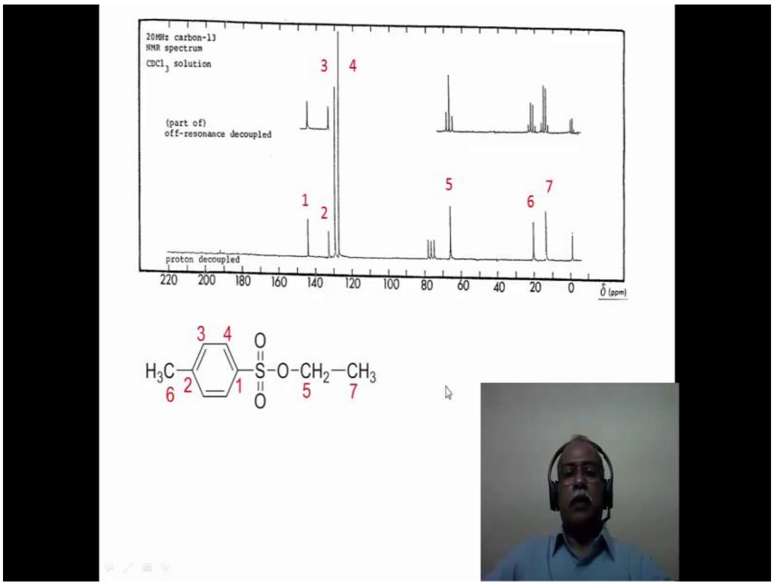

The carbon 13 spectrum can also be easily assigned. The 2 low intense peak would be the ipso peak; one correspond to, the one that is attached to the sulfonyl group, will have the higher delta value. The second one attached to the methyl group will have a lower delta value; and the CH carbons, which are the 3 and 4, can be assigned like this; adjacent to the sulfonyl, would be 4, and adjacent to the 3, would be essentially, this particular assignment will be correct. Now, the CH 2 which is attached to the oxygen, will come around 65 p p m or so. In this particular case, it comes around 67, 68 p p m or so. The CH 3, which is aromatic CH 3, comes around 20 p p m and the terminal CH 3 would come around 10 to 12 p p m, which is this particular peak that is seen here. And, off resonance spectrum also very clearly tells us that, this is a CH 2; this is a CH 3 and this is a CH 3 p.

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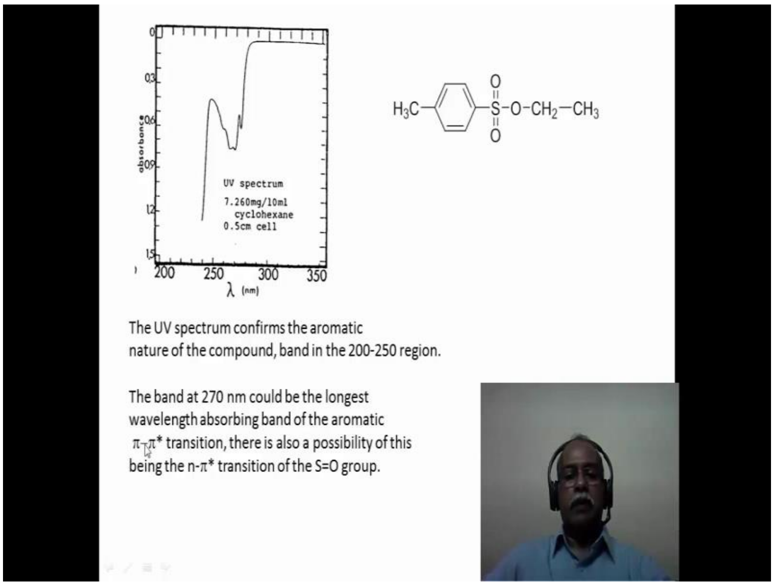

The UV spectrum confirms the aromatic nature of the compound, band in the 200-250 region.

The band at 270 nm could be the longest wavelength absorbing band of the aromatic π-π* transition, there is also a possibility of this being the n-π* transition of the S=O group.

So, essentially, carbon 13 spectrum, as well as the proton NMR spectrum, mass spectrum are easily fitted into this particular structure. The only thing that is remaining is the UV visible spectrum. The UV visible spectrum confirms that, it is an aromatic compound, because of the large absorption that is happening between 200 to 350 nanometer. The absorption maximum is so high that, you do not see it very clearly; it goes beyond the scale that is shown here. There is a band at 270; this could be the longest wavelength absorption band of the aromatic pi - pi; so, a transition. Or, it could also possibly be the n pi star transition because of the SO group; we are not very sure about it.

Most likely, this is the longest wavelength absorbing aromatic pi pi star transition. One can easily calculate the epsilon value, and find out, whether it is a forbidden transition, or an allowed transition. This is something, exercise, we have already done. The mass is given; the molecular weight is also known from the mass spec; the cell dimension is given here, and the absorption corresponds to about 0.7 or 0.6, 0.875 or so, in this particular case. So, using Beer-Lambert's law, one can calculate the epsilon value, which you can do it yourself.

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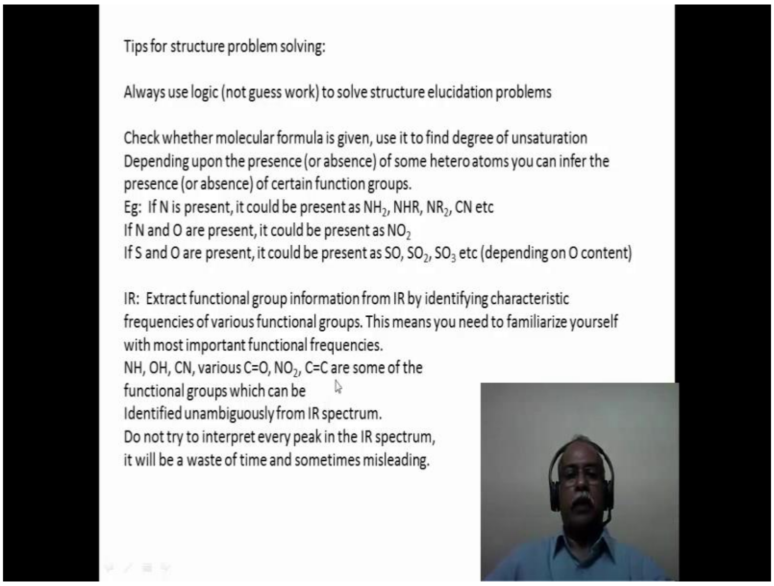

Tips for structure problem solving:

Always use logic (not guess work) to solve structure elucidation problems

Check whether molecular formula is given, use it to find degree of unsaturation
Depending upon the presence (or absence) of some hetero atoms you can infer the presence (or absence) of certain function groups.
Eg: If N is present, it could be present as NH_2, NHR, NR_2, CN etc
If N and O are present, it could be present as NO_2
If S and O are present, it could be present as SO, SO_2, SO_3 etc (depending on O content)

IR: Extract functional group information from IR by identifying characteristic frequencies of various functional groups. This means you need to familiarize yourself with most important functional frequencies.
NH, OH, CN, various C=O, NO_2, C=C are some of the functional groups which can be
Identified unambiguously from IR spectrum.
Do not try to interpret every peak in the IR spectrum,
it will be a waste of time and sometimes misleading.

Now, let us see, if we can give you some tips for the problem solving session. First of all, always use logic to solve the structures of, structure elucidation problem; do not do any kind of a guess work; because, guess work can actually lead you in the wrong direction, and end up in a mess of things, which is not easy to solve afterwards. Check whether the molecular formula is given; if it is given, use it to find the degree of unsaturation. Depending on the presence, or absence of hetero atom, you can infer the presence, or absence of certain functional group; for example, if nitrogen is present, you can come to the conclusion that, it might be an NH 3 group, or NH R group, or a tertiary amine, or a cyano functional group.

If both nitrogen and oxygen are present, if there are two oxygens present in the nitrogenous compound, it could as well be a NO 2, which you can confirm from the infrared spectrum. If sulphur and oxygen are present, like we saw in the earlier example, it could be SO, SO 2, or SO 3, depending upon how many sulphurs, and how many oxygen atoms are present in the system. In the infrared spectrum, extract the functional group information by identifying characteristic frequencies of various functional group. This means that, you need to familiarize yourself with most functional group frequency; it comes only with practice. However, simple functional groups like a NH, OH, CN, carbonyl, NO 2 and C double bond C are unmistakable functional group, which can be unambiguously identified from the NMR spectra, sorry, from the infrared spectrum; corresponding stretching frequency will be intense peaks. So, one can easily identify them. Please do not worry about interpreting every little peak in the infrared spectrum; it would be a waste of time, and sometimes, it could be also misleading. So, try to interpret only the most obvious peaks in the infrared spectrum, and see, whether you can support it from other spectroscopic data also.

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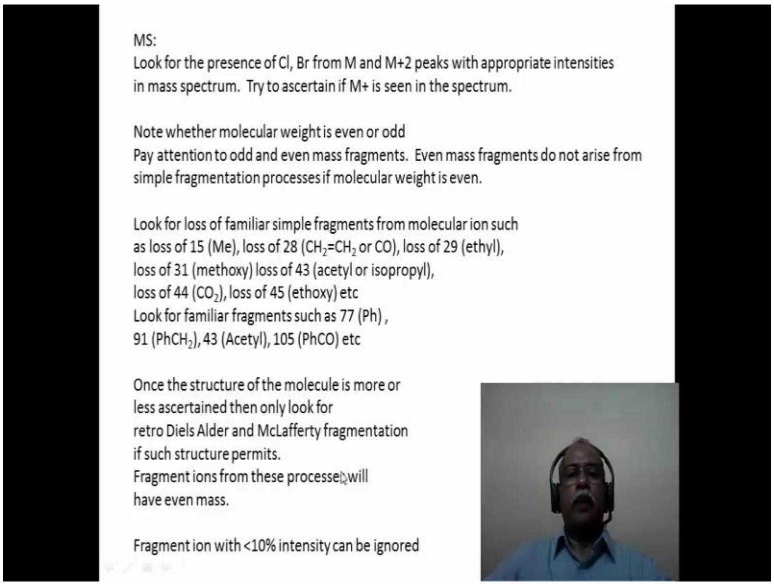

MS:

Look for the presence of Cl, Br from M and M+2 peaks with appropriate intensities in mass spectrum. Try to ascertain if M+ is seen in the spectrum.

Note whether molecular weight is even or odd

Pay attention to odd and even mass fragments. Even mass fragments do not arise from simple fragmentation processes if molecular weight is even.

Look for loss of familiar simple fragments from molecular ion such as loss of 15 (Me), loss of 28 (CH_2=CH_2 or CO), loss of 29 (ethyl), loss of 31 (methoxy) loss of 43 (acetyl or isopropyl), loss of 44 (CO_2), loss of 45 (ethoxy) etc

Look for familiar fragments such as 77 (Ph), 91 ($PhCH_2$), 43 (Acetyl), 105 (PhCO) etc

Once the structure of the molecule is more or less ascertained then only look for retro Diels Alder and McLafferty fragmentation if such structure permits.

Fragment ions from these processes will have even mass.

Fragment ion with <10% intensity can be ignored

In the mass spec, look for the presence, or absence of chlorine, because in the presence of chlorine, or presence of bromine can be inferred by their appearance of M and M plus 2 peak with appropriate intensities. If it is a chlorinated compound, M and M plus 2 will be, 1 is to, sorry, 3 is to 1 ratio.

If it is a bromine compound, it will be 1 is to 1 ratio. From the intensity ratios and the number of multiplets that you see in the M and M plus 2, M plus 4 region, you can even tell how many bromines and chlorines are present in the system. Try to ascertain, if the molecular ion is seen in the spectrum also. Normally, you can assume that, the highest m by z value peak is the molecular ion peak. Sometime, this could be a wrong assumption also. If the molecule fragments very rapidly, if your molecular ion is not seen, this could be leading to some kind of a misinterpretation. If the molecular ion peak is seen, see whether it is an even number, or odd number. If it is, pay attention to the odd, or even mass fragments also. Even mass fragments do not arise from simple fragmentation process, if the molecular weight is a even molecular weight. This is extremely important. If it is a odd molecular weight, you come to the conclusion, there is a odd number of nitrogen, or a single nitrogen present in the system.

And, look for familiar fragmentations in the, from the molecular ion; for example, a loss of 15 would correspond to methyl; a loss of 28 would correspond to either a loss of ethylene, or a CO; loss of 29 would correspond to an ethyl group loss; loss of 31 would be a methoxy, and so on. So, these are losses which are easy to identify from the molecular ion peak for simple compounds. Look for familiar fragments also; having m by z value 77 would correspond to phenyl; 91 would correspond to benzyl; 43 would correspond to acetyl; 105 would correspond to phenoxyl.

So, this kind of fragments can also be easily identified, if you can recognize these fragments very readily from the molecular weights. Once the structure of the molecule is more or less ascertained, then, you look for the more complex fragmentation patterns, like retro Diels Alder and McLafferty rearrangement, and so on. Fragments arising from these processes will be even mass, provided the molecular weight is also even in this compounds. So, do not straightaway look for McLafferty rearrangement in the mass spectrum, unless you are sure that, it is a carbonyl compound, or a compound which has a structural unit, which is capable of undergoing McLafferty rearrangement and so on. That is a caution one need to do. Again, do not interpret the entire mass spectrum; peaks which have less intensity, less than 10 percent, can be ignored in the mass spectrum.

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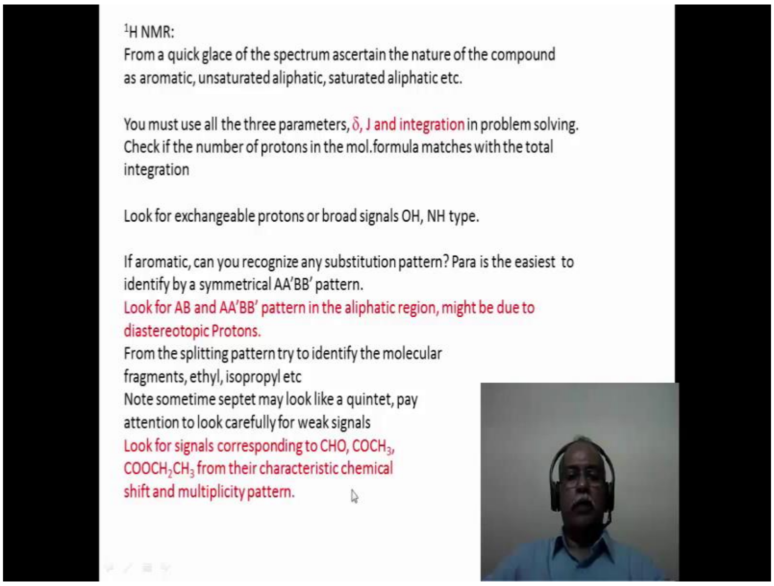

^1H NMR:
From a quick glace of the spectrum ascertain the nature of the compound as aromatic, unsaturated aliphatic, saturated aliphatic etc.

You must use all the three parameters, δ, J and integration in problem solving.
Check if the number of protons in the mol.formula matches with the total integration

Look for exchangeable protons or broad signals OH, NH type.

If aromatic, can you recognize any substitution pattern? Para is the easiest to identify by a symmetrical AA'BB' pattern.
Look for AB and AA'BB' pattern in the aliphatic region, might be due to diastereotopic Protons.
From the splitting pattern try to identify the molecular fragments, ethyl, isopropyl etc
Note sometime septet may look like a quintet, pay attention to look carefully for weak signals
Look for signals corresponding to CHO, $COCH_3$, $COOCH_2CH_3$ from their characteristic chemical shift and multiplicity pattern.

Proton NMR spectrum probably gives the most valuable information about the structure of the compound. So, from a quick glance of the spectrum, ascertain the nature of the compound to be either aromatic unsaturated, or saturated aliphatic compound, because they have very characteristic region, between 7 to 8 p p m is aromatic; between 5 to 7 p p m is unsaturated compound, aliphatic compounds; saturated compounds typically come between 1 p p m and 5 p p m or so, depending on how many substituents are present in the system. You must use all the 3 parameters. One can get the parameter of delta, J, as well as integration value. Do not try to ignore any of these parameters; use all of them in conjunction, to do, in problem solving session. Check, if the number of protons in the molecular formula matches with the total integration, because, each integration would correspond to a certain number of hydrogen. If you add up all the integration, that should match the molecular formula of the particular component, the number of hydrogen present in the molecular formula.

Look for exchangeable hydrogen. They are easy to identify, because, they are very broad, and usually the D 2 O exchange information is often given in the spectral data. If the compound is aromatic, see, if you can recognize the substitution pattern. para substitution is the easiest to recognize, because it is a symmetrical AA prime BB prime pattern. We have also seen some examples of the meta substitution pattern. If we can recall this pattern during the problem solving session, it will be nice to figure out the number of substituents. Look for AB, or AA prime BB prime pattern in the aliphatic region also; this might be because of a diastereotopic type of hydrogen. From the splitting pattern, try to identify the molecular fragment; for example, ethyl group, isopropyl groups are easy to identify from the splitting pattern. Note that, sometimes, the septet may look like a quintet; pay attention to very weak signals in the multiplets, so that, the end lines are not missed in the NMR spectrum.

Also, look for signals which would correspond to CHO group, which will come around 9 to 10, or 9 to 11 p p m; CH 3 CO peak, for example, which will come around 2 to 2.5 p p m or so; COO C 2 H 5, p p m, this would come around 4.1 p p m or so. These are very characteristic chemical shift and multiplicity pattern, correspond to certain functional group, which should not be missed in the NMR spectrum.

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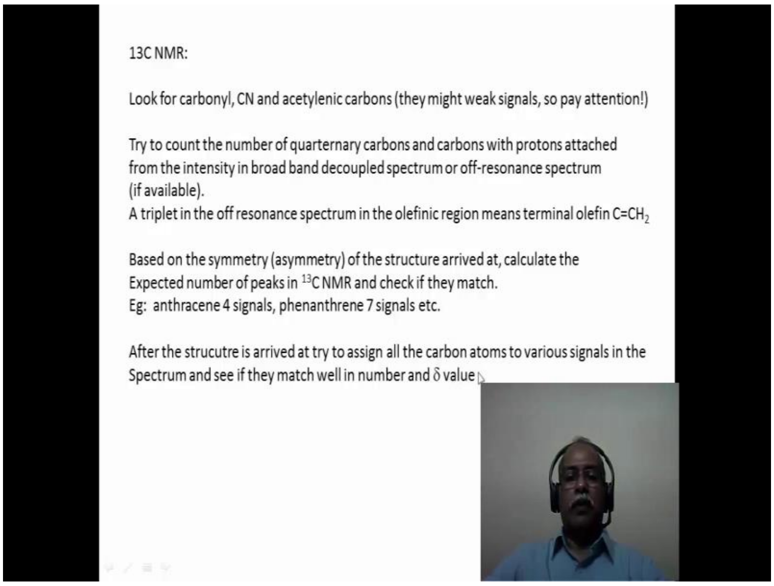

13C NMR:

Look for carbonyl, CN and acetylenic carbons (they might weak signals, so pay attention!)

Try to count the number of quarternary carbons and carbons with protons attached from the intensity in broad band decoupled spectrum or off-resonance spectrum (if available).
A triplet in the off resonance spectrum in the olefinic region means terminal olefin $C=CH_2$

Based on the symmetry (asymmetry) of the structure arrived at, calculate the Expected number of peaks in ^{13}C NMR and check if they match.
Eg: anthracene 4 signals, phenanthrene 7 signals etc.

After the strucutre is arrived at try to assign all the carbon atoms to various signals in the Spectrum and see if they match well in number and δ value

Carbon 13 spectrum, one can look for low intensity peaks corresponding to carbonyl, cyano and acetylenic carbon, because these, only carbon 13 gives signature for this kind of functional group, besides the infrared spectrum. One can always use the carbon 13 data, as well as the infrared data, to confirm the presence, or absence, of this kind of functional groups. Try to count the number of quaternary carbons, and the number of carbons that has proton attached to it, based on the intensity. Usually, the quaternary carbons are low intense in nature, and the carbons attached to hydrogens are high intensity in nature. And, if off-resonance spectrum is available, make use of the information of the off-resonance spectrum. In the off-resonance spectrum, if there is a triplet in the olefinic region, you can be very sure that, it is because of a terminal olefine, with the C double bond CH 2 kind of a functional group being present there. Mostly, symmetry reduces the number of signals in the carbon 13 spectrum.

One can tell for sure from the symmetry, how many signals are to be expected for a given compound. The example is, anthracene has 4 signals, whereas, phenanthrene has 7 signals, because phenanthrene is less symmetric than the anthracene molecule, for example. So, check for the number of signals that is expected, based on the structure, and the number signals that is actually seen in the NMR spectrum. After the structure is deduced, try to assign all the carbon atoms to various signals, and see, if they match well in number, as well as the delta value. In other words, the number of signal expected, and the actual signals seen, should match each other. The number of carbons that is seen in the structure that is arrived at, should have the sufficient number of signals in the carbon 13 spectrum. Watch out for overlapping signals; sometimes, this is indicated in the spectrum; often, this is difficult to figure this out, in the aromatic region. So, be careful about that.

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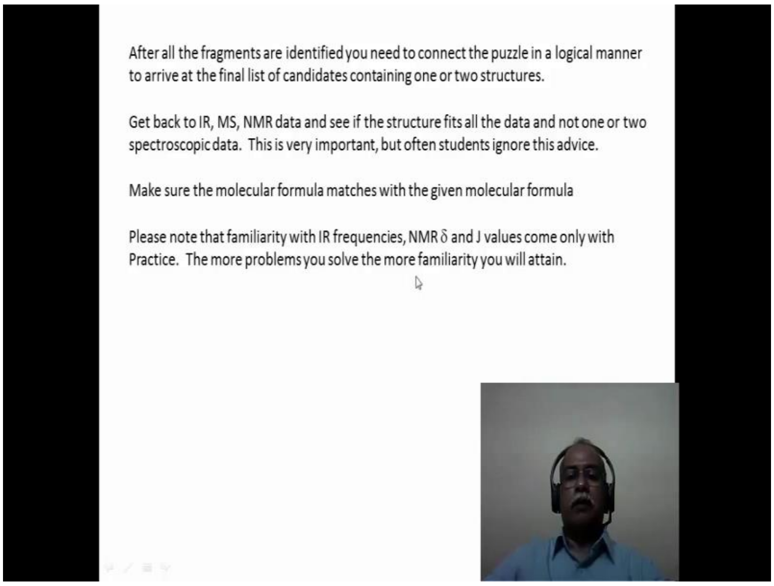

After all the fragments are identified you need to connect the puzzle in a logical manner to arrive at the final list of candidates containing one or two structures.

Get back to IR, MS, NMR data and see if the structure fits all the data and not one or two spectroscopic data. This is very important, but often students ignore this advice.

Make sure the molecular formula matches with the given molecular formula

Please note that familiarity with IR frequencies, NMR δ and J values come only with Practice. The more problems you solve the more familiarity you will attain.

After all the fragments are identified, one needs to connect the puzzle in a logical manner, to arrive at the final list of candidates, containing one or more structures. In other words, you do not rule out any structure without any logical reason; just a, do not assume, that is a wrong structure; try to analyze the structure; get back to the infrared, mass spec and the NMR data, and see, if the structure fits all the data, not just 1 or 2 spectroscopic data. Once the range of spectroscopic data is given, the final structure should match all the spectroscopic data. It should not match only mass spec, and not NMR; only IR, and not the NMR; that kind of a argument is not a valid argument. It is very important, because, often times, the students do not go back and check the spectroscopic data for the structure that they arrive at.

Often, they can come to some wrong conclusion, and make mistakes in this structural assignment, if you do not go back and check it properly. Make sure, the molecular formula matches with the given molecular formula; the structure that you arrive at, it has a molecular formula; it should match with the given molecular formula. If the molecular formula information is given, please note that, familiarity with infrared spectrum is, spectral frequency, NMR delta, J value, comes only with practice. So, the more problems you try to solve, the more familiar you will become, in solving the structure elucidation problems carefully. I hope these tips are very useful to you. Good luck in your examination.

Thank you very much for your kind attention.