Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 28
Infrared Spectroscopy - Problem solving based on IR spectroscopy

Hello, welcome to module-28 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. In the previous 3 modules, we discussed about infrared spectroscopy, the fundamental aspects of it and the application aspects of infrared spectroscopy also we discussed. We will make this as a tutorial session, in other words a problem-solving session based on infrared spectroscopy along.

Now, one does not always use only infrared spectroscopy to do any kind of a structural elucidation problem solving. The purpose of this particular module is to make you familiar with the infrared spectra, so that various functional groups can be identified and in terms of interpretation of the infrared spectrum, the familiarity builds; yes, built up during the course of this tutorial session.

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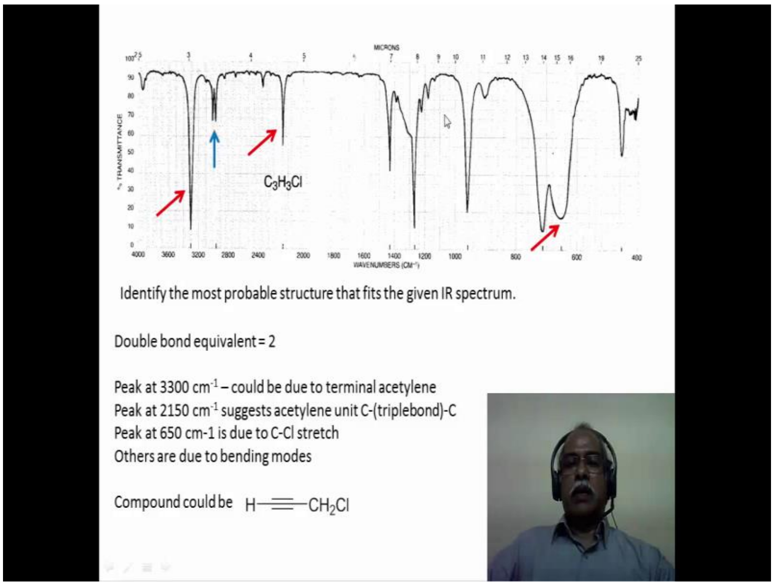

C_3H_3Cl

Identify the most probable structure that fits the given IR spectrum.

Double bond equivalent = 2

Peak at 3300 cm^{-1} – could be due to terminal acetylene
Peak at 2150 cm^{-1} suggests acetylene unit C-(triplebond)-C
Peak at 650 cm-1 is due to C-Cl stretch
Others are due to bending modes

Compound could be $H{-}{\equiv}{-}CH_2Cl$

Now, here is the question, there is a infrared spectrum of a compound with the molecular formula C3H3Cl, what is the most probable structure that will fit this particular data? Now, as you see the infrared spectrum, you need to understand the characteristic features of the infrared spectrum in this particular case. There is a sharp peak around 3250 or so, in this particular region and there is another sharp peak around 2100 and something, 2200 and some frequency is also there is a sharp peak and there are other peaks also present in this particular system.

So, let us first focus on this particular peak which corresponds to the 3300 inverse centimeter peak and the 2150 inverse centimeter peak also. Now, this particular peak could suggest that this is a terminal CH, terminal acetylene CH stretching frequency. Please, remember that among the various hybridization, CH stretching frequency the SPCH stretching frequency comes at the highest frequency, then comes the SP 2 and then finally, comes the SP 3. So, it could be that this is because of an acetylenic CH stretching frequency, their terminal acetylene CH stretching frequency. If that suspicion is true, then you should also have a C triple bond C stretching frequency. Indeed, you do a have C triple bond C stretching frequency coming at 2115 inverse centimeter, which is the part of the 3 triple bonds C acetylenic unit in this particular case.

The molecule does not have any kind of OH or NH, so one cannot interpret this by mistake to OH or a NH kind of a stretching frequency because they also come in the same region. For example, a secondary amine can easily come in this region as a sharp peak like this and that is not the case because the molecule does not possess any kind of nitrogen. Molecule also has a double bond equivalence of 2, in other words it is an unsaturated system with the double unsaturation, so your terminal acetylene can actually satisfy the unsaturation of this particular molecule is gas.

Now, finally, the molecule has a chlorine, so the C-Cl should be seen somewhere. The C-Cl is actually seen as a stretching frequency in the region of 650 inverse centimeter. This peak is most likely due to the C-Cl kind of a stretching. So, based on the problem, this is a very simple molecular formula, one can jawed down the various possibilities and rule out one after the other. In doing so, for example, we look at the terminal CH of an acetylenic peak and a C triple bond C of an acetylenic peak and a C-Cl of the acetylenic peak is also seen in this particular case. So, based on this we suggest that this is actually propargyl chloride is the structure of the compound that would most likely fit the spectral data in this. The arrow indicating, the blue arrow indicating this particular frequency which is looking like a doublet, could be because of the symmetrical and asymmetrical stretching of the CH of the CH 2 group. In other words, the SP 3 CH stretching frequency comes in this region somewhere around 2900 inverse centimeter or so. So, this is how one tries to analyze and interpret the NMR infrared spectrum for a given molecular formula, first to find the degree of unsaturation and look at the most prominent peaks. These peaks are also prominent peaks but then they probably come in the bending region of this molecule, so one does not interpret this in very detailed manner as far as the bending regions are concerned.

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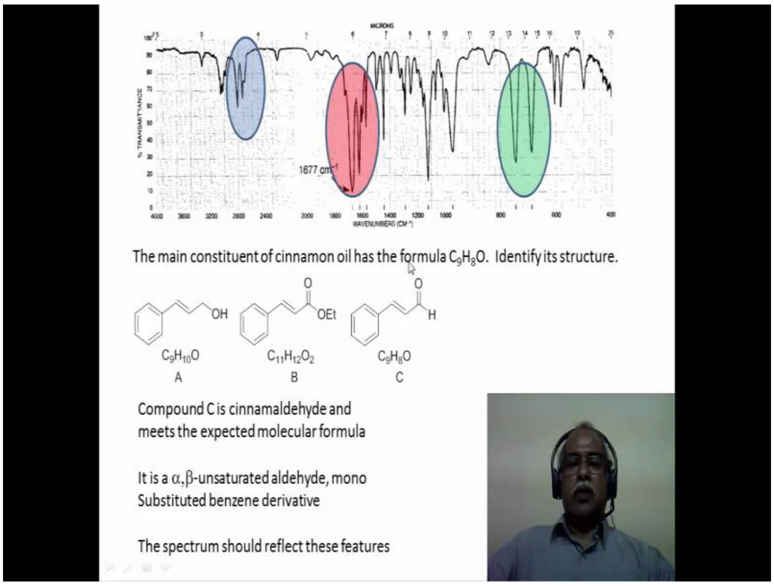

The main constituent of cinnamon oil has the formula C_9H_8O. Identify its structure.

$C_9H_{10}O$
A

$C_{11}H_{12}O_2$
B

C_9H_8O
C

Compound C is cinnamaldehyde and meets the expected molecular formula

It is a α,β-unsaturated aldehyde, mono Substituted benzene derivative

The spectrum should reflect these features

Now, the problem is stated here. The main constituent of cinnamon oil has the formula C 9 H 8 O. Identify it is structure? One needs to know, what is the main constituent of cinnamon oil? It could be cinnamaldehyde, it could cinnamyl alcohol, it could be cinnamate ester or it could be cinnamic acid all the cinnamon based systems are written here, except cinnamic acid is not written here. Now, among this formula A B C molecule if you look at, the one that is cinnamaldehyde corresponds to C9H8O. So, the molecular formula is satisfied for the cinnamaldehyde structure.

But, let us see whether the infrared spectrum also satisfies this particular structure. One can easily rule out A and B because it does not fit in the molecular formula that is given. So, the cinnamaldehyde probably best fits the structure. Compound C is cinnamaldehyde, and it meets the expected molecular formula that is good and it is alpha beta unsaturated aldehyde and it is also a mono substituted benzene derivative. So, what one need to look in the NMR, sorry, not the NMR I keep telling NMR. This IR spectrum is that one need to look at the aldehyde stretching frequency for an alpha beta unsaturated carbonyl functional group and one needs to look at whether it is a disubstituted benzene derivative, in terms of the out of plain bending mode of the mono substituted derivative. One can also look for the CH stretching frequency of the aldehyde in the infrared spectrum.

Now, if you look at the highlighted areas clearly, it tells you that there is an aldehyde functional group both an alpha beta unsaturated aldehyde functional or carbonyl stretching frequency 1677 corresponds to that. In fact, we can also see the C double bond C stretching frequency by the side of it because it is an alpha beta unsaturated system. And, the CH stretching frequency of the aldehyde which comes around 28 inverse centimeter as 2 line pattern is also very clearly seen and finally, the mono substituted benzene derivative which has out of plane bending modes in this particular feature is also reflected. So, the spectrum actually reflects the features that would satisfy this particular molecule to be the correct molecule as far as the major constituent of the cinnamon oil is concerned is cinnamaldehyde.

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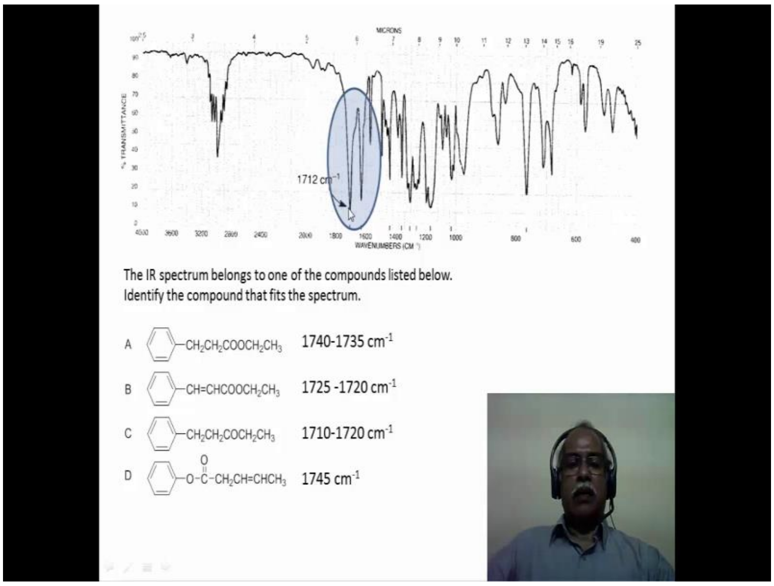

The IR spectrum belongs to one of the compounds listed below.
Identify the compound that fits the spectrum.

A $-CH_2CH_2COOCH_2CH_3$ 1740-1735 cm^{-1}

B $-CH{=}CHCOOCH_2CH_3$ 1725 -1720 cm^{-1}

C $-CH_2CH_2COCH_2CH_3$ 1710-1720 cm^{-1}

D $-O-\overset{O}{\overset{\|}{C}}-CH_2CH{=}CHCH_3$ 1745 cm^{-1}

Now, there are 4 options given, one need to choose the correct option which will fit in this particular infrared spectrum. In other words, the IR spectrum belongs to one of the compounds listed below, identify the compound that fits the spectrum? Now, let us look at this spectrum, the structure of this compound. This is a saturated ester and this is also a ester, but it is an alpha beta unsaturated ester, this is a saturated ketone and this one is a alpha beta unsaturated ester plus an unsaturation is also there. So, if one were to look for an alpha beta unsaturated ester, the saturated ester comes around 1750-1740 inverse centimeter frequency and if it were to be an alpha beta unsaturated system it will come around 1720 or so. So, one can expect the saturated ester to be ruled out because the carbonyl stretching frequency is actually seen at 1712, so this can be ruled out.

One can also easily rule out the alpha beta unsaturated carbonyl ester functional group because this will not be less than 1720 or so. One can easily rule out this particular ester because this is a unsaturation is conjugating with the lone pair of oxygen here it would in fact, increase the frequency compared to the base value for an alpha beta unsaturated system. So, this is a saturated ester functional group which is also 1745, which is higher than what is observed. So, the one that fits the most is this saturated ketone which is the expected to come around 1710 or 1720 for a linear acyclic carbonyl functional group which is a ketone, 1712 seem to match the spectrum correctly. So, this particular region essentially, because it is an aromatic system the C double bond C is also seen here. So, one can very clearly tell rule out the possibility of A B C to be the wrongs, A B D to be the wrong structure. So, the correct structure is C for that particular spectrum.

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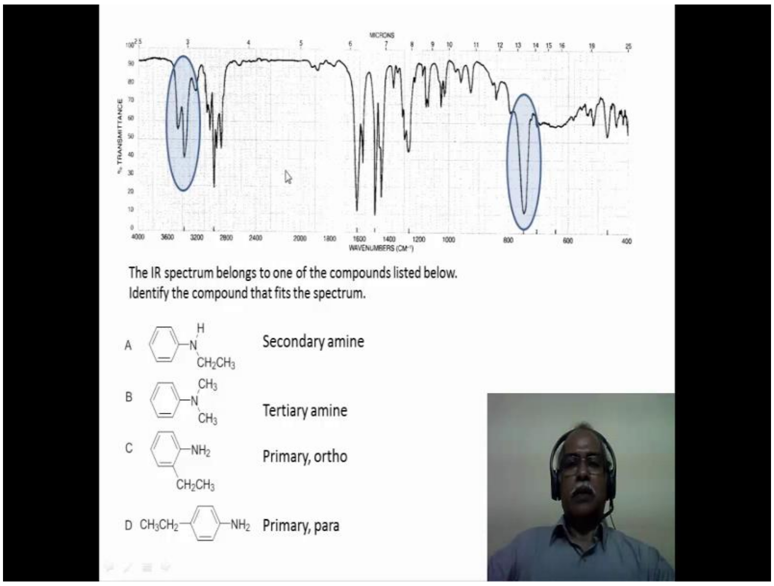

The IR spectrum belongs to one of the compounds listed below.
Identify the compound that fits the spectrum.

A Secondary amine

B Tertiary amine

C Primary, ortho

D Primary, para

Let us move on. Now, there are 4 structures again given here, with 1 infrared spectrum. One has to match the spectrum to 1 of these structures that is given here. Now, this is a secondary amine and this is a tertiary amine. So, secondary amine should give only 1 peak in this region, but there are 2 peaks here, so one can easily rule out that it is a not a secondary amine. Tertiary amine should not give any kind of a NH stretching frequency, this is NH stretching and this is the CH stretching region of the infrared spectrum, because all of them are amino compound we can conclude that one has to have a primary amine to a C=Count for the doublet kind of a structure that is given here. The NH primary amine gives both asymmetric as well as symmetric stretching frequency that is why it comes at a doublet, which will be absent in the secondary amine as well as the tertiary amine.

So, A and B can be straight away ruled out on the basis of the NH stretching frequency being a doublet. So, only C and D seem to fit the criteria. Now, how do we decide whether it is a C or the D? That one has to depend upon the out of plane bending mode.

If it is paradise substituted derivative of this kind there will be only one band out of plane bending band. If it is in the ortho substituted derivative like this, there will be 2 bands or more bands, so on that basis one can rule out c also. So, the correct structure most likely is D, which is para amino ethyl benzene for this particular spectrum.

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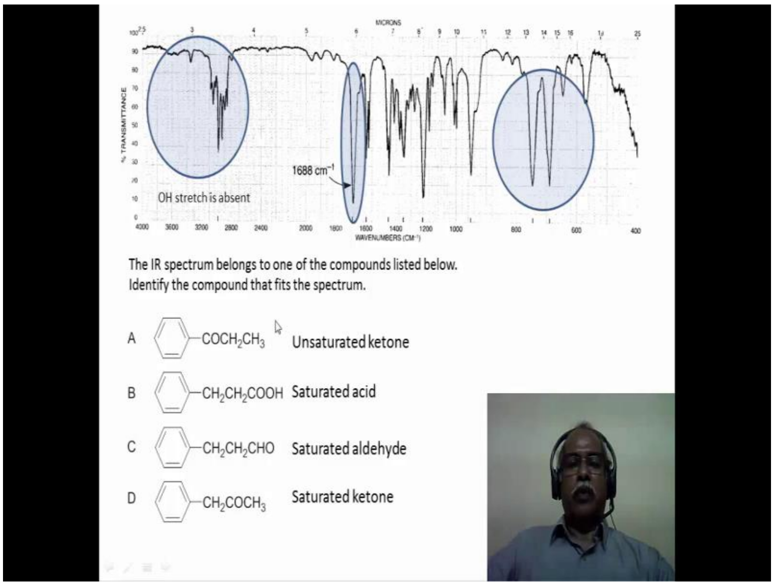

OH stretch is absent

1688 cm^{-1}

The IR spectrum belongs to one of the compounds listed below. Identify the compound that fits the spectrum.

A —$COCH_2CH_3$ Unsaturated ketone

B —CH_2CH_2COOH Saturated acid

C —CH_2CH_2CHO Saturated aldehyde

D —CH_2COCH_3 Saturated ketone

Now, this infrared spectrum again, there are again 4 structures given here and we have to fit in one of these structures to this particular infrared spectrum. Now, if you look at the compounds this is an alpha beta unsaturated ketone and this is a saturated acid, so one can easily rule out the saturated acid because there is no OH functional group in the molecule. So, the absence of the OH stretching frequency in this region essential rules out the possibility that it is a carboxylic acid. So, B is ruled out. It could be a saturated aldehyde, but then this is not a saturated aldehyde value, remember saturated aldehyde should come around 1720 or 1710 this is around 1688. So, saturated ketone and saturated aldehyde can also be easily ruled out.

So, the only option is that you have a alpha beta unsaturated ketone, this is propiophenone is the molecule. Propiophenone has a frequency around 1688 because it is an alpha beta unsaturated ketone. Because, it is a mono substituted benzene derivative it also has the out of plane bending modes which is coming in this particular region.

So, these are the most prominent observation that one needs to make in order to distinguish the fact that the carboxylic acid can be straight away ruled out is based on the fact that there is no OH stretching frequency. Carboxylic acids invariably give a very broad band in this particular region for OH stretching frequency which is absent. And, one can also rule out on the basis of the fact it is not an aldehyde, because the aldehyde CH stretching frequency is also not seen, which should come around 2800 inverse centimeter or so. The correct structure for this infrared spectrum is A, which is propiophenone in this particular case.

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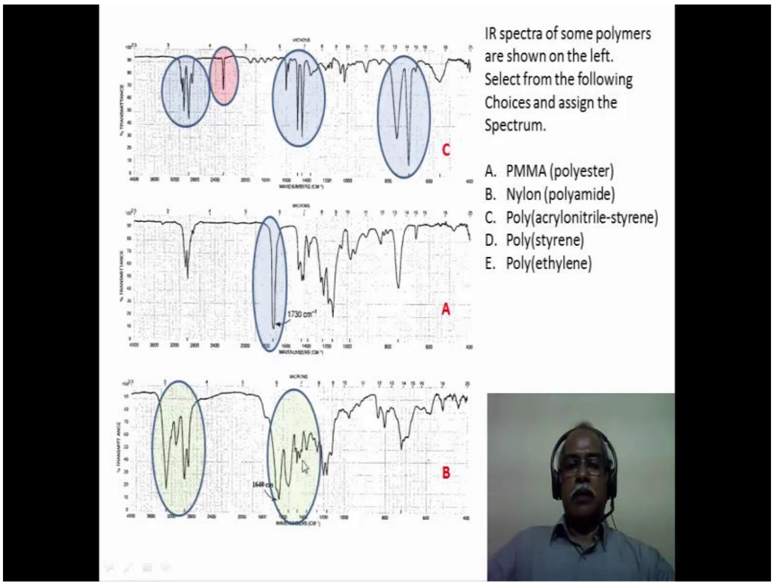

IR spectra of some polymers are shown on the left. Select from the following Choices and assign the Spectrum.

A. PMMA (polyester)
B. Nylon (polyamide)
C. Poly(acrylonitrile-styrene)
D. Poly(styrene)
E. Poly(ethylene)

Here there is another problem. The IR spectrum, there are 3 IR spectra given here and they belong to one of these polymers. Each one belongs to one of these polymers, so one need to match the IR spectrum with the correct identification of the polymer structure. The polymers given are PMMA, which is poly methyl methacrylate which is a ester polymer, it is a saturated ester polymer. Nylon, which is a polyamide you should have an amide stretching frequency for this one. Poly acrylonitrile-styrene co polymer, Poly styrene polymer, Poly ethylene polymer. Now, if you look at poly ethylene polymer this is a saturated CH 2-CH 2-CH 2 kind of a chain. It is like a paraffin oil or like a nujol kind of a system is what one should see. So, if you look at this spectrum, the prominent peaks are CH peaks here and C double bond C peaks in this particular region and again out of plane bending kind of a mode vibration is what is seen here. So, these are the prominent features. So, in fact, polystyrene will fit in this particular system, but look carefully this particular band here, this band which is coming around 20, this is coming around 2200 or so corresponds to probably nitrile kind of a functional groups.

So, one is unmistakably one should identify this as a nitrile functional group. The only polymer in this series A B C D that has a nitrile functional group is the acrylonitrile styrene polymer. So, it has a signature of both styrene as well as the acrylonitrile chain, which is a co polymer in this particular case. Suppose, if this peak which is highlighted in red is missing, one can easily if say that this belongs to poly styrene kind of spectrum. One can rule out polyethylene in all of these, because polyethylene will have a nujol kind of a spectrum it will have only a CH stretching frequency. Since, it has C trouble bond C CO bond stretching frequencies, one can straight away rule out E as an option, D as an option is also ruled out now, because the carbonyl functional groups are there in the other 2 spectra. So, one can rule out D also in this particular case. So, D and E are ruled out, one has to deal with A B C. Now, we have identified this compound to be C which is the poly acrylonitrile styrene.

Let us come to the next spectrum which has a carbonyl stretching frequency at 1730. 1730 is a saturated ester carbonyl stretching frequency, so most likely PMMA, in other words poly methyl methacrylate polyester is responsible for this particular stretching frequency. Then we are left only with the nylon, which is an amide. Amide has 2 carbonyl stretching frequency and also has a NH stretching frequency. In fact, one can see the NH as well as the CH stretching frequency in the region between 2800 to 3200 or so in this region, which is characteristic region for the NH and CH. And then, there are 2 intense band which are the amide bands; amide band 1 and amide band 2 are seen very clearly in the case of polyamide. So, the assignment is that this is poly acrylonitrile styrene co ploymer, this is corresponding to PMMA which is poly methyl methacrylate ester polymer and finally, B nylon which is a polyamide polymer is in this particular spectrum.

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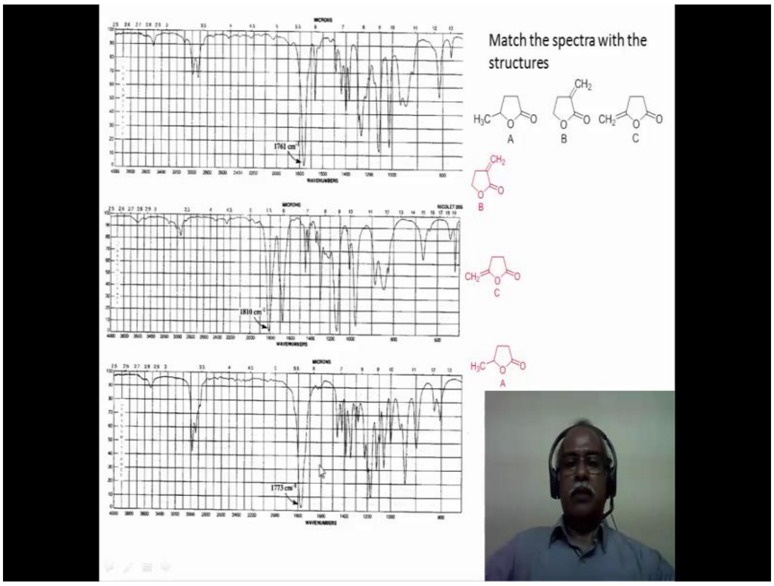

Match the spectra with the structures

Here is another problem. 3 IR spectra are given and 3 structures A B C are also given, one needs to match the spectra with the corresponding structure. Now, if you look at A B C this is a saturated gamma lactone, alpha beta gamma lactone. This is alpha beta unsaturated gamma lactone and this is also unsaturated lactone, but except the unsaturation is in conjugation with oxygen lone pair of the lactone rather than the carbonyl functional group. So, based on the discussion we had in the earlier module this would have the highest stretching frequency of the carbonyl stretching frequency in the IR spectrum, then comes the saturated carbonyl stretching frequency of the saturated lactone and then comes the alpha beta unsaturated lactone carbonyl stretching frequency.

The stretching frequencies are marked for the carbonyl stretching in the IR spectrum this is 1761, this is 1810 and this is 1773. So, based on the argument C should be this one which has the highest stretching frequency of 1810's, so C corresponds to the middle spectrum here, A corresponds to the spectrum which is in the bottom which is 1773 and B corresponds to the alpha beta unsaturated system which has the lowest one around 1761. So, the assignments are this is B, this is C and this is A, in terms of these, so all you need to do in this particular case is to look at carbonyl stretching frequency alone, nothing else is necessary in fact, to identify this system. In fact, the saturated, if you look at the alpha beta unsaturated system, you have the additional C double bond C in this C double bond C is here and here the C double bond C is here, whereas this does not have any band corresponding to a C double band C. So, this is clearly the saturated system unmistakably one can say on the basis of C double bond O and the absence of C double bond C.

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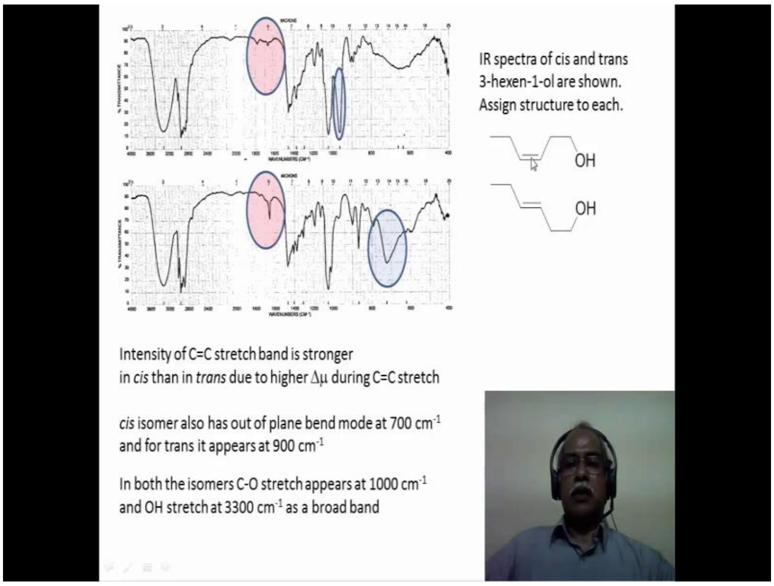

IR spectra of cis and trans 3-hexen-1-ol are shown. Assign structure to each.

Intensity of C=C stretch band is stronger in *cis* than in *trans* due to higher $\Delta\mu$ during C=C stretch

cis isomer also has out of plane bend mode at 700 cm^{-1} and for trans it appears at 900 cm^{-1}

In both the isomers C-O stretch appears at 1000 cm^{-1} and OH stretch at 3300 cm^{-1} as a broad band

Now, the IR spectrum of cis and trans cyclohexenol is given here. One need to assign which one corresponds to which. Now, one needs to understand the concept that when you have a stretching happening in the case of the cis isomer there will be maximum change in the dipole moment compared to a trans isomer. So, when you have comparison of cis and trans isomer you look at the C=C stretching here. C=C stretching will be maximum in the case of the intensity wise it will be a higher, in the case of cis isomer rather than the trans isomer.

So, this information is necessary to understand in order to have the assignment to be done properly. The intensity of the C double bond C stretch is stronger in the case of cis then in the case of trans due to the higher change in the dipole moment, during the C double bond C stretching. The cis isomer also has the out of plane bending mode 700, this many people may not know this, but it is very useful information. Whereas the trans has the out of plane bending around 900 inverse centimeter. Both the C-O stretch appear at 1000 inverse centimeter as well as OH stretch appear at 3300. In other words, the OH stretching frequency as well as the C-O stretching frequency which is over here, they are not very useful because both of them has hydroxy functional group and both of them will have the same C-O stretching functional group also.

But, if you look at the highlighted region here which corresponds to the C double bond C stretching region which is around 1600 inverse centimeter or so, the intensity here is much higher compare to the intensity here. So, that would put this to be the cis isomer and addition to that use the information out of plane bending for the cis is around 700 inverse centimeter and for the trans around 900 inverse centimeter. So, combine this 2 factors, the top spectrum corresponds to the trans isomer and the bottom spectrum definitely corresponds to the cis isomer because this has a higher intensity of the C double bond C.

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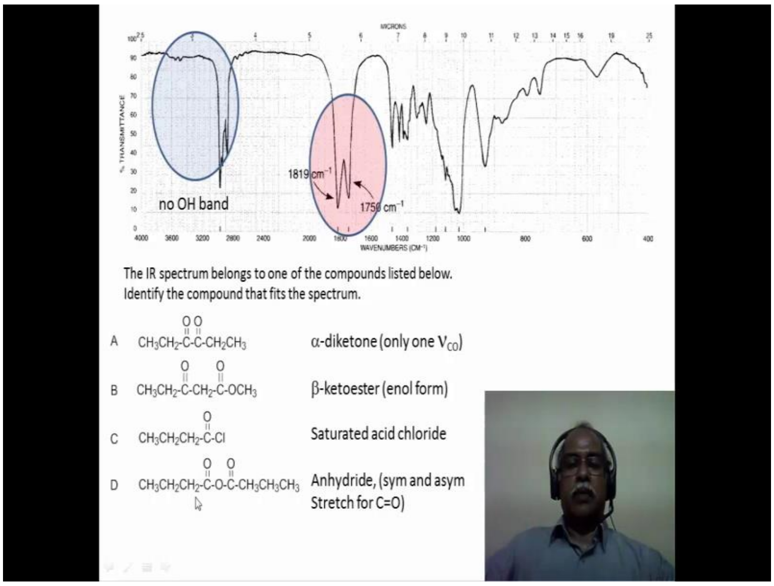

The IR spectrum belongs to one of the compounds listed below. Identify the compound that fits the spectrum.

A	$CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_3$	α-diketone (only one ν_{CO})
B	$CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3$	β-ketoester (enol form)
C	$CH_3CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$	Saturated acid chloride
D	$CH_3CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3CH_3CH_3$	Anhydride, (sym and asym Stretch for C=O)

Another problem, interesting problem on based on the carbonyl functional group assignment. You have alpha diketone, remember alpha diketone give only 1 band in the infrared spectrum, they do not give 2 bands because there are 2 carbonyl functional group. They have identical stretching frequency, so only 1 band is obtained. In the case of beta keto ester, beta keto ester exists in the enol form also. So, they will also give the

OH stretching frequency if it were to be present. The fact that there is no OH stretching frequency here rules out the beta keto ester as the possibility in this particular case. Acid chlorides also give only 1 stretching frequency, remember the anhydride which gives the 2 stretching frequency one corresponding the symmetric, the other one corresponding asymmetric stretching frequency.

So, when you see a band like this around 1800-1750 region, definitely, it is because of an anhydride. So, one can straight away rule out the possibility of A B C for this spectrum. The structure D corresponds to the spectrum perfectly in terms of the fitting of the data for the 2 carbonyl stretching frequency in the region 1820 and 1750, corresponding to asymmetric and symmetric stretching frequencies of the anhydrides system in this case. So, no OH band, so rule out B. 2 bands in the infrared carbonyls stretching frequency in the 1800 region definitely, corresponds to the anhydride system.

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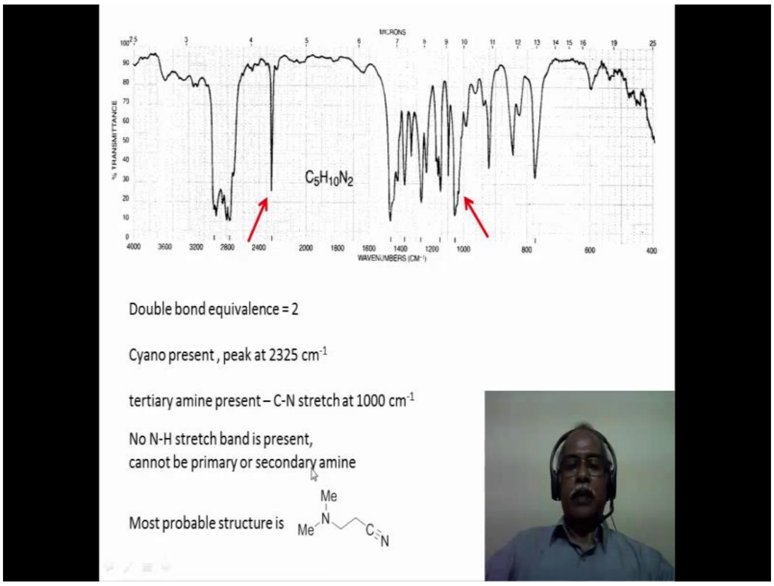

Double bond equivalence = 2

Cyano present , peak at 2325 cm^{-1}

tertiary amine present – C-N stretch at 1000 cm^{-1}

No N-H stretch band is present,
cannot be primary or secondary amine

Most probable structure is

Here is a problem. A molecular formula is given, from the molecular formula you can tell this molecule has an degree of unsaturation of 2 and what is the name of the compound? Is what we are asking here. The double bond equivalence is 2. There is a cyano peak present here because there is a nitrogen present here, you will look for amine or the cyano. Cyano is definitely here because it is coming around 23 25 inverse centimeter. So, that corresponds to the cyano functional groups. So, one of the nitrogen is cyano functional group and you can also look whether there is a NH stretching frequency. NH is absent, so it cannot be primary amine or secondary amine. But, you cannot rule out a tertiary amine possibility, in order to identify whether it is a tertiary amine one can always look at the C-N stretching region. C-N stretching is fairly strong, this here for example, the C-N stretching region.

So, it could be a tertiary amine. So, based on the molecular formula being a simple C 5 molecular formula, if you rule out the primary amine, secondary amine as well as the acetylene as an unsaturation, you come up with the structure which corresponds to something like this. This is 3 NN dimethyl amino, propionitrile is the name of the structure of the compound that is shown here. This is most likely the structure which fits the molecular formula, which also fits the degree of unsaturation, which also fits the presence of a carbonyl, sorry, nitrile functional group with a C-N stretching frequency which gave a clue that it could to be an amine also because there are 2 nitrogen present here.

It cannot be a dinitrile compound because of the 2 nitrogen because then the degree of unsaturation will be much higher than 2. It will become 4 for example. You cannot have more than 1 nitrile functional group. So, the other nitrogen has to be an amino functional group. If the absence of NH frequency gave the clue that it could be a tertiary amine, so the tertiary amine is put in this particular to fit the molecular formula C 5, this is a most likely structure that corresponds to this particular spectrum.

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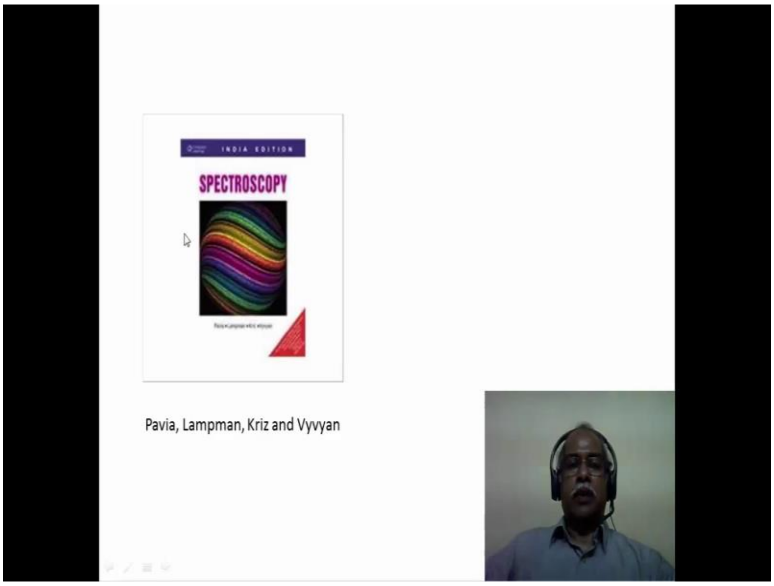

INDIA EDITION

SPECTROSCOPY

Pavia, Lampman, Kriz and Vyvyan

So, all the spectra are recorded that is shown in this particular problem solving session is taken from this book.

I would like to thank you very much for your kind attention.