Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 26
Infrared Spectroscopy or Vibrational Spectroscopy

Hello, welcome to module 26 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. We will continue with the Infrared Spectroscopy, in this module we will look at examples of OH, NH and CH stretching frequencies in the particular region in the infrared spectrum.

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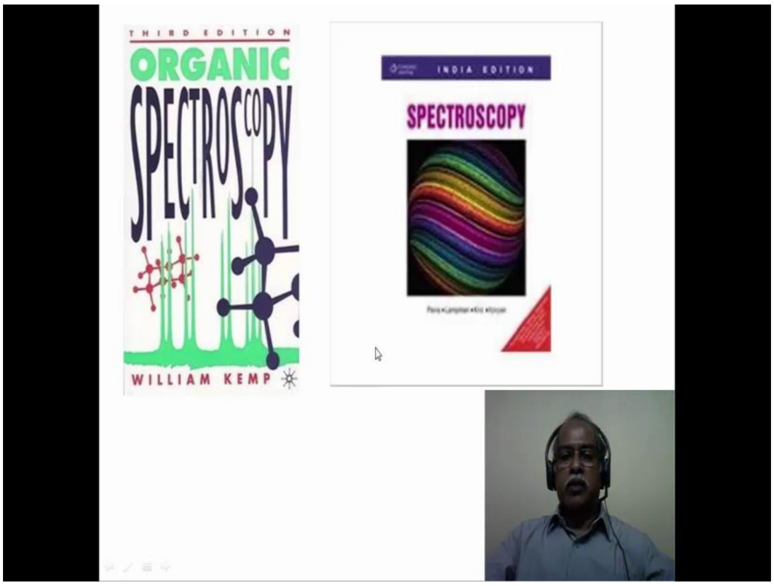

For the purpose of illustration several spectra were taken from these 2 books that is Organic Spectroscopy by William Kemp and Spectroscopy by Pavia and others and I am grateful to these 2 sources for the illustration purposes this spectra have been taken from this 2 books.

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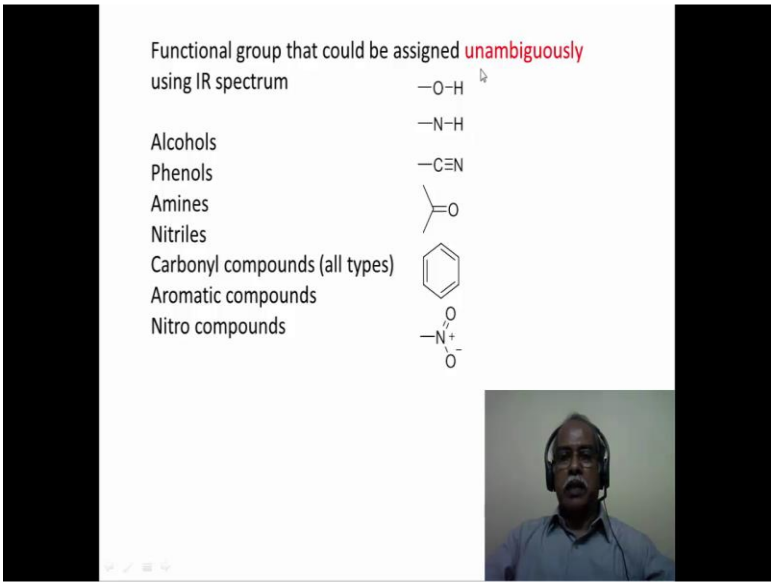

Functional group that could be assigned unambiguously using IR spectrum

- Alcohols
- Phenols
- Amines
- Nitriles
- Carbonyl compounds (all types)
- Aromatic compounds
- Nitro compounds

Now, the functional group that could be easily or unambiguously assigned from an infrared spectrum are typically Alcohols and Phenols, Amines, Nitriles, Carbonyl compounds, Aromatic compounds and then Nitro compounds. Although, the infrared spectra give a wealth of information about a lot of other functional group, from the organic chemist point of view these are the functional group that one normally looks for in the infrared spectrum the presence or absence of these functional groups can be unambiguously assigned.

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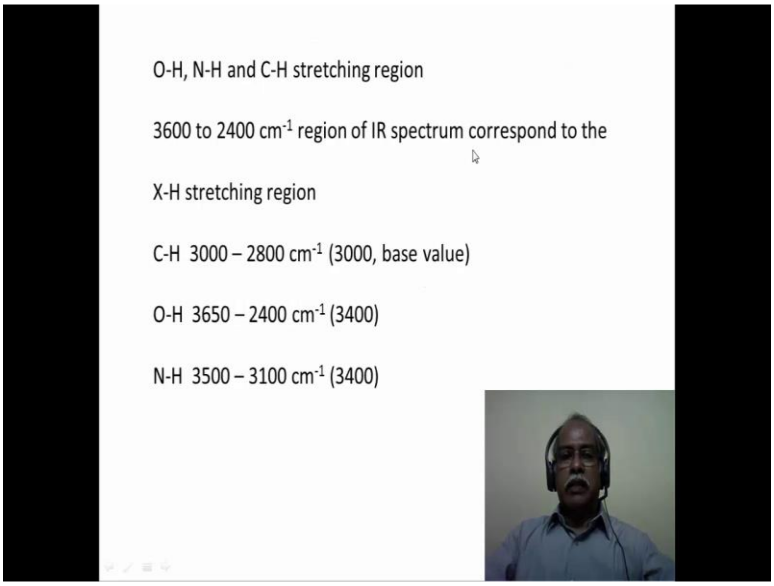

O-H, N-H and C-H stretching region

3600 to 2400 cm^{-1} region of IR spectrum correspond to the

X-H stretching region

C-H 3000 – 2800 cm^{-1} (3000, base value)

O-H 3650 – 2400 cm^{-1} (3400)

N-H 3500 – 3100 cm^{-1} (3400)

Now, the O-H, N-H, C-H stretching region is a very unique region. This is in the left hand side of the infrared spectrum starting from 3600 inverse centimeter to 2400 inverse centimeter. It is a fairly broad region, but within this region 1 can classify the C-H, O-H and N-H frequencies based on the masses of the atoms that are attached to it namely carbon, oxygen and nitrogen as the case.

In the infrared spectrum the C-H region is typically from 3300, the base value is about 3000, but it extends from 3300 to some 2800 are so. The O-H region is typically between, 3650 to 2400 or so, with the base value corresponding to about 3400 inverse centimeter. The N-H region corresponds to 3500 to 3100 typically the base value essentially same as the O-H base value.

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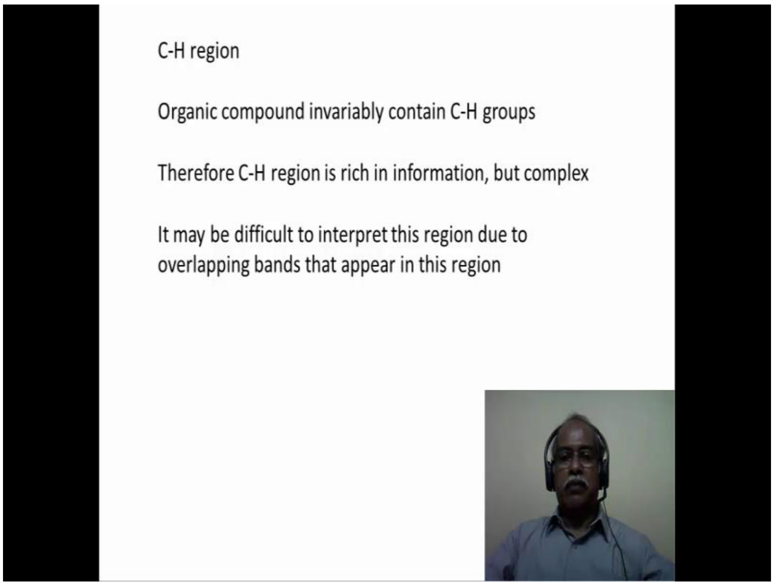

C-H region

Organic compound invariably contain C-H groups

Therefore C-H region is rich in information, but complex

It may be difficult to interpret this region due to overlapping bands that appear in this region

Now, let us have look at the C-H region. Almost all the organic compound will have a C-H functional group because particularly unless it is a completely fluorinated or completely halogenated substance they will have the C-H group present. Therefore, the C-H group region is fairly rich in information but highly complex in nature in terms of analysis. It may be difficult to interpret this region due to overlapping bands that appear in this region. In other words, since the O-H, C-H and N-H appear in nearly the same region interpretation of the region can be somewhat difficult for the C-H region. Let us have a look at the various types of C-H groups that one can have in the organic molecule.

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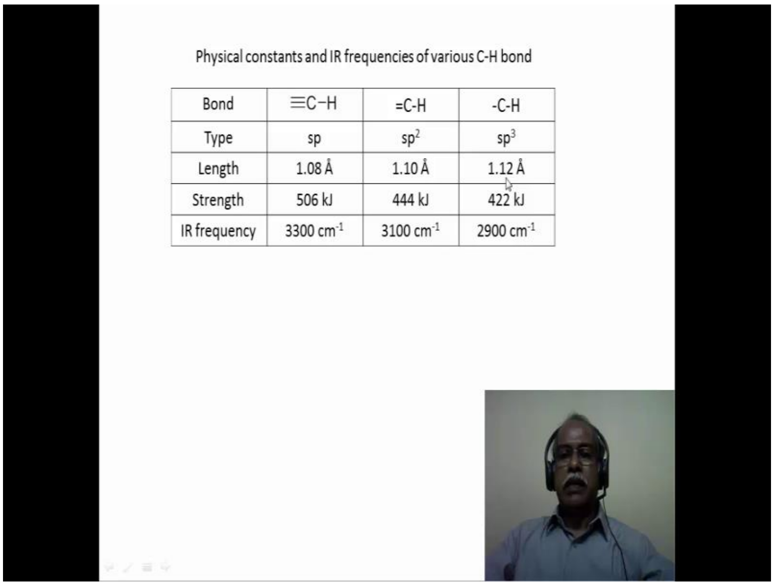

Physical constants and IR frequencies of various C-H bond

Bond	≡C−H	=C-H	-C-H
Type	sp	sp^2	sp^3
Length	1.08 Å	1.10 Å	1.12 Å
Strength	506 kJ	444 kJ	422 kJ
IR frequency	3300 cm^{-1}	3100 cm^{-1}	2900 cm^{-1}

This is something we have already seen depending upon the bond strength the stretching frequency keeps increasing with the increasing bond strength. In other words an acetylenic C-H, vinylic C-H and an alkynic C-H is compared here. The alkynic C-H is around 2900 inverse centimeter. Whereas, the alkenic C-H is about 3100 inverse centimeter and an acetylenic C-H is 3300 inverse centimeter in terms of the stretching frequency of the C-H bond. This C-H bond in the acetylenic unit in the strongest bond therefore, it comes at the highest stretching frequency value. As you can see here from the strength of the bond, this is the strongest bond and this is next strongest bond. This is a weakest bond among the three, which is also reflected in terms of the bond length of the C-H bond that is indicated here.

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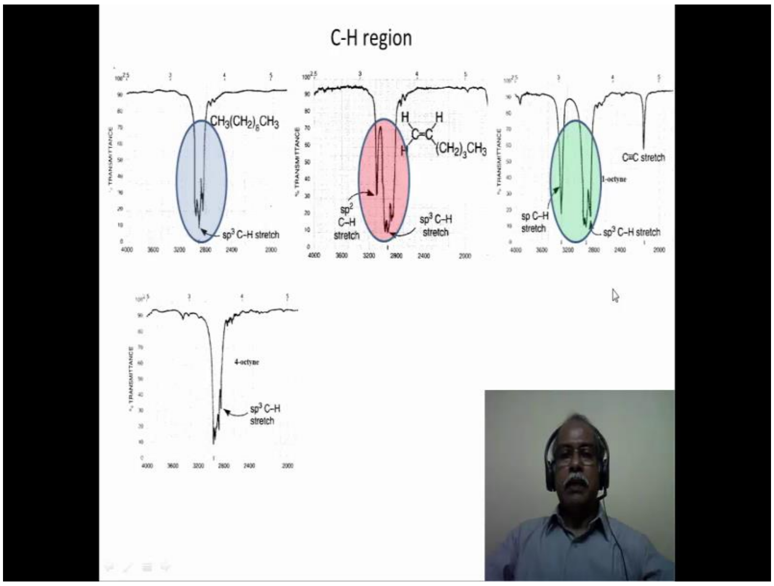

C-H region

These are examples of spectral region corresponding to the C-H region. The entire infrared spectrum is not shown only the region from 4000 to 2000 is shown because that essentially covers the C-H region. In this region if you look carefully, if it an alkane this is a linear alkane, this is a decane molecule. The C-H region essentially contains only sp 3 C-H, so that comes as a bunch of peaks in the region narrow region of about 2800 or 2900 inverse centimeter. In other words, it is coming from 2800 to some 3100 inverse centimeters as multiple peaks that are seen corresponding to this C-H stretching of the sp 3 C-H carbon hydrogen, sp 3 carbon hydrogen stretching is what is seen in this region.

Now when you take an alkene, this is actually octene, 1 octene as an example shown here this as both sp 2 C-H as well as sp 3 C-H. One can clearly see the sp 2 C-H to come at a higher frequency or higher energy region compare to the rest of the C-H which nearly looks as this one here, so this corresponds to the sp 3 hybridized C-H stretching frequency and this sharps singlet kind of a thing that is seen here at a higher frequency region correspond to the sp 2 C-H stretching frequency. Now when you go to terminal acetylene, the terminal acetylene in this is particular case is 1 octyne is taken as the example. The terminal acetylene C-H comes at even higher frequency. The olefinic C-H comes around 30, 150 or so, whereas the terminal acetylene peak comes around 3200 or so in this particular case. So, among the C-H sp 3 C-H comes as the lowest sp 2 at a higher and sp even higher in terms of the frequency where it is being observed. If you are taking an internal alkane, which does not possess the C-H terminals, C-H acetylenic C-H, this particular band is missing here essential because this is internal acetylene. Internal acetylenes do not have acetylene hydrogen therefore, that particular band is very clearly missing in the case of 4 octyne compare to the spectrum of 1 octane which has the C-H corresponding to the sp C-H stretch of the C-H functional group.

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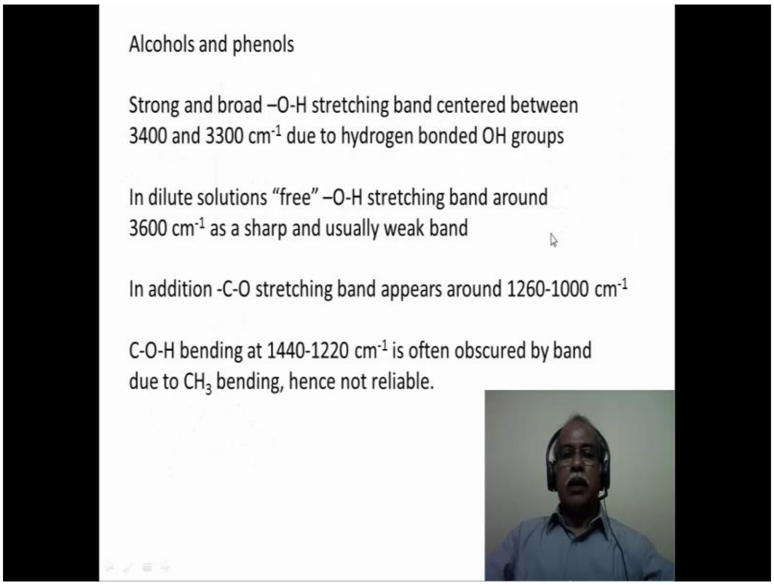

Alcohols and phenols

Strong and broad –O-H stretching band centered between 3400 and 3300 cm^{-1} due to hydrogen bonded OH groups

In dilute solutions "free" –O-H stretching band around 3600 cm^{-1} as a sharp and usually weak band

In addition -C-O stretching band appears around 1260-1000 cm^{-1}

C-O-H bending at 1440-1220 cm^{-1} is often obscured by band due to CH_3 bending, hence not reliable.

Now, let us go to alcohol and phenol, we are talking about though O-H stretching frequency. O-H stretching frequency is a very characteristic feature in infrared spectrum; it is very strong and broad. In case of the O-H which is hydrogen bonded in nature, it is centered between 3400 to 3300 due to hydrogen bonding it is generally very broad in nature and also very intense signal.

Now, dilute solutions can see, you can see the free O-H in dilute solution. The stretching band corresponding to the free O-H comes at a higher frequency value compare to 3400 value this is 3600 and generally it is very sharp and usually a weak band is what is seen for a free O-H because most of the hydroxy containing compounds exist as hydrogen bonded system.

In order to see the free O-H 1 has to considerably dilute the solution that is one of the reason why this band is fairly weak in dilute solution. In addition to the O-H stretching frequency one should also see the C-O stretching frequency, which appears in 1260 to 1000 inverse centimeter. This is a characteristic region for the C-O single bond stretching frequency, so the O-H bending also comes in the region of 1440 to 1220 but it is often obscured by the band due to the CH 3 bending hence it is not a reliable thing. So, the reliable information that one can get for an alcohol or phenol kind of a molecule is a stretching frequency, whether it is hydrogen bonded O-H stretching frequency or a free O-H stretching frequency depends on a dilution of the sample bond and C-O stretching frequency which appears around 1260 to 1000 inverse centimeter.

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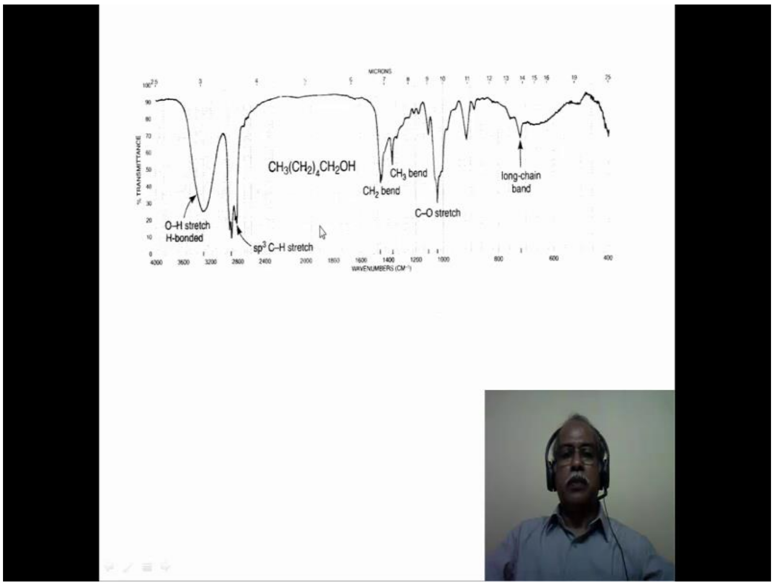

Here, is a spectrum of this particular alcohol which is hexanal. Hexane 1 all for example, this is a neat sampled in other words the liquid thin film is taken between 2 sodium chloride plate in the form of a very thin film and the infrared spectrum is measured. One can see a very broad band in the region between 3100 to 3100 to 3300 or so 3400 or so with the maximum around 30 to 50 or so in this particular region and this corresponds to the O-H stretching frequency. Then you have the C-H stretching frequency which is coming at a lower delta sorry lower frequency values with the around 2800 inverse centimeter. Then the C-O stretching is a very characteristic region around low 1 this is

1100 so this should be around 1050 or so is the region were the C-O stretching, single stretching, single bond C, single bond O stretching frequency comes. So, this is a characteristics spectrum of an alcohol kind of sample.

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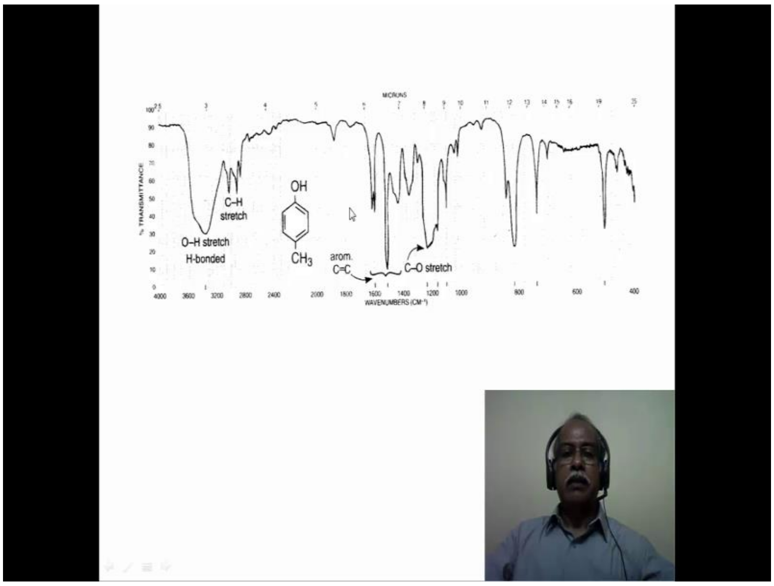

In the case of phenol also you will have the sp 2 C-H band you can see the difference gap between these 2 bands are fairly high because this is around 2800, when it is moving to sp 2 closes up to a 3000 region it is closer to the O-H peak for example. The O-H broad peak that is seen here is essentially because of the hydrogen bonded OH stretching frequency of the phenolic compound here. In addition to the C-O stretch which comes here because of the C double bond, C being present in this phenolic molecule, one can also see the C double bond c stretching. So, essentially this region which is divide of the C double bond C stretching frequency tells you that this is probably an aliphatic kind of an alcohol, Whereas this is probably either olefin containing alcohol or an aromatic unit containing alcohol because of the fact you have the C double bond C as well as the C single bond OH stretching frequency appearing in this region which characteristic features of an aromatic phenolic kind of compound.

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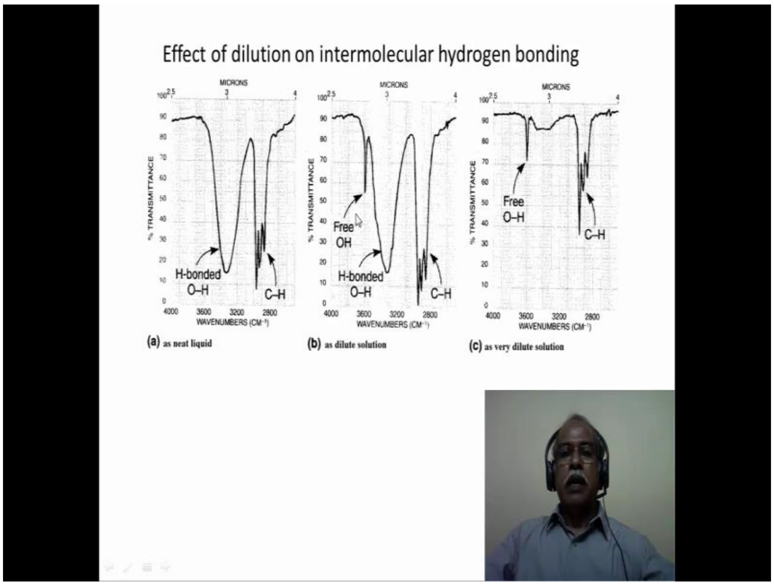

Effect of dilution on intermolecular hydrogen bonding

(a) as neat liquid

(b) as dilute solution

(c) as very dilute solution

In order to see the free hydrogen, free O-H stretching frequency one need to really look at the spectrum in a very dilute solution. Typically, carbon tetra chloride is used as a solvent. 3 different spectra of the same sample is given here, it is an alcohol sample. This is a neat liquid is what is used for the sampling. Here, a dilute solution is used and here a very dilute solution is used to dilute. Dilute and very dilute is only a relative term in this particular case. One can very clearly see in the neat spectrum a broadband because of the O-H stretching frequency corresponding to the hydrogen bonded O-H stretching frequency is what is seen here plus you can also see the C-H stretching frequencies in this particular region.

When you have a dilute sample there are 2 bands which are appearing, 1 is a sharp band at a higher frequency and then you are usual broadband like what you saw here around 3300 as the maximum, same frequency around 3300 is a maximum that you see here. Maximum intensity in terms of the transmittance, for example, this is essentially because of the free O-H and this is essentially because of the hydrogen bonded O-H. When you have a mixture of free O-H as well as the hydrogen bonded O-H, this is a characteristic feature by which you can identify the free O-H and the hydrogen bonded O-H. When it is further diluted to a very dilute solution the hydrogen bonding are broken and you do not have much of the hydrogen bonded system here, now you have only a free O-H. The weakness of the intensity of this particular band is essentially because it is a very dilute solution as you can see here, even the C-H band has become weaker in terms of the intensity because of the dilution nature of this particular sample that is being investigated.

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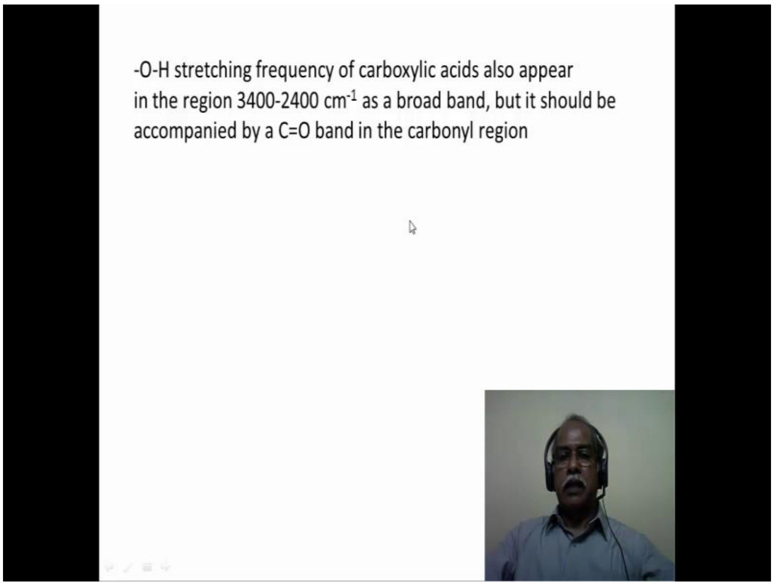

-O-H stretching frequency of carboxylic acids also appear in the region 3400-2400 cm^{-1} as a broad band, but it should be accompanied by a C=O band in the carbonyl region

There is also a O-H stretching frequency in carboxylic acid that appear in the same region as the phenolic and the hydroxy functional group. Only difference is this is much broader because carboxylic acids are typically hydrogen bonded in nature both in solid as well as in dispersion's, but only thing is that in the case of a phenol and alcohol there will not be a C double bond O stretching frequency, whereas in the case of a carboxylic acid, in addition to the O-H stretching frequency one should also observe a carbonyl stretching frequency in the carbonyl region.

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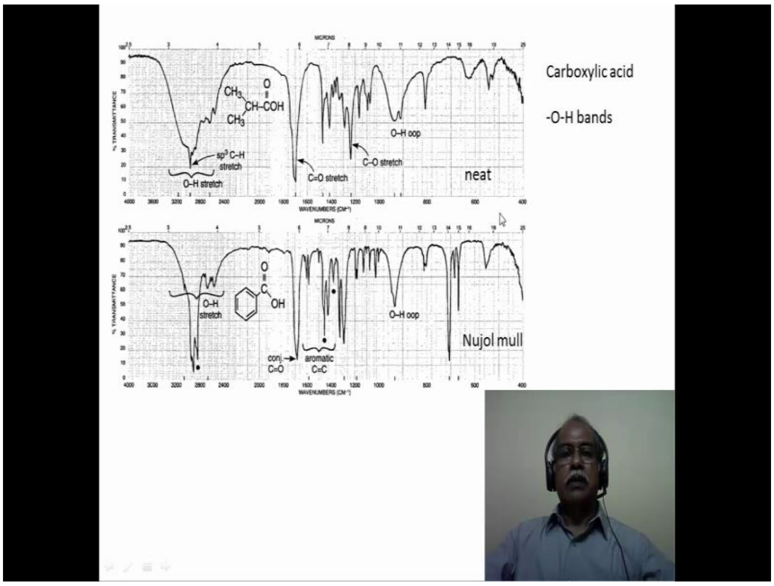

Carboxylic acid

-O-H bands

Now, this is the example of a isobutyric acid sample. One can see a very broad envelope of O-H which is even masking the C-H peaks also along with it, so it is a fairly broad peak is what is seen for the O-H consisting of this entire envelope of a stretching frequencies which also masks the C-H stretching frequency which you can barely see as spike on broadband of the O-H stretching frequency. Carbonyl stretching frequency is also there that is it is a carboxylic acid derivative. This is a spectrum of benzoic acid; this is actually in the dispression in a Nujol mull, whereas this is neatly taken as the neat sample. In other words the liquid sample is taken neat and the solid sample is dispersed in Nujol mull.

The peak corresponding to the nujol mull are identify by a dot, you see the dot here which is corresponding to the C-H stretching frequency of the nujol and this is a C double bond stretching frequency of the nujol and this is also because of the nujol for example. So, the O-H stretching frequency essentially is the broad stretching frequency that you see in this region corresponding to the carboxylic acid O-H and the conjugated carbonyl that what it is coming around 1700 or so in the case of the benzoic acid, as a carbonyl stretching frequency as well as the O-H stretching frequency corresponding to the carboxylic acid.

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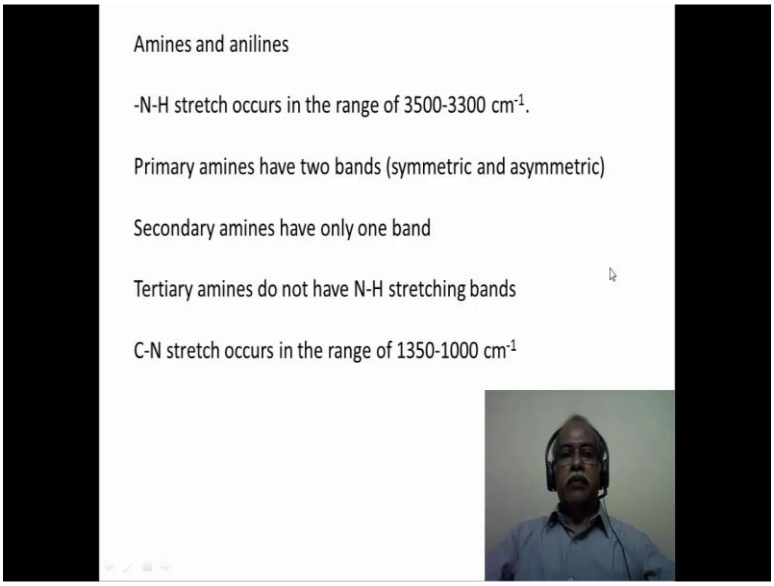

Amines and anilines

-N-H stretch occurs in the range of 3500-3300 cm^{-1}.

Primary amines have two bands (symmetric and asymmetric)

Secondary amines have only one band

Tertiary amines do not have N-H stretching bands

C-N stretch occurs in the range of 1350-1000 cm^{-1}

In the case of Amines and Anilines, N-H stretching frequency occurs at slightly higher frequency compared to the O-H stretching frequency. Primary amines will have 2 bands this is a very characteristic feature of primary amines because of the symmetric and the asymmetric nature of the N-H stretching frequency. Secondary amines on the other hand will have only 1 band corresponding to N-H stretching frequency. Tertiary amines do not have N-H frequency because there is no N-H bond in the tertiary amines. In addition to the C-H sorry, in addition to the N-H stretching frequency 1 should also observe the C-N stretching frequency at 1350 to 1000 inverse centimeter in the case of amines.

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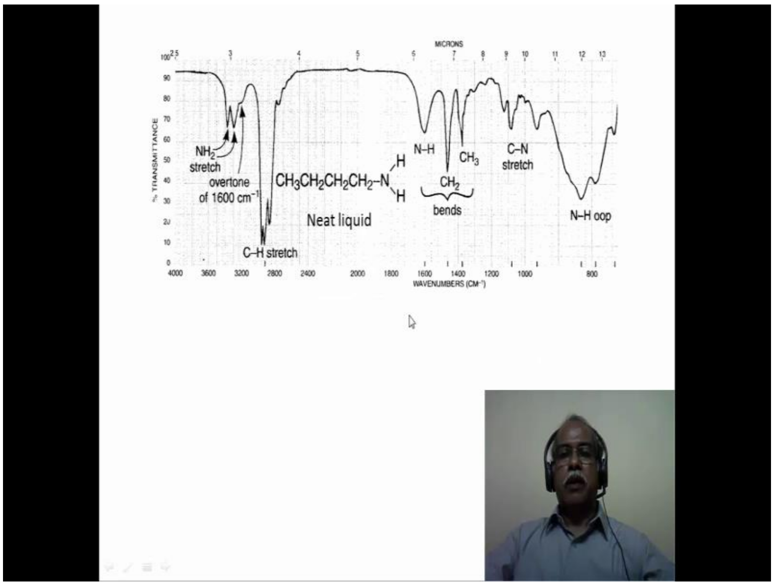

This is an example of butyl amine, normal butyl amine it is a primary amine. In the primary amine this is measured as a neat liquid for example, and one can see in the N-H region a doublet kind of a thing this is the pattern that one need to look for when we are looking for a primary amine kind of a system. And this is a C-H region and this is N-H region very distinctly delineated in this particular case. In addition to that, the C-N stretching frequency also appears in this case for example, around 1050 or 1150 or so is the C-N stretching frequency which is appearing in this case.

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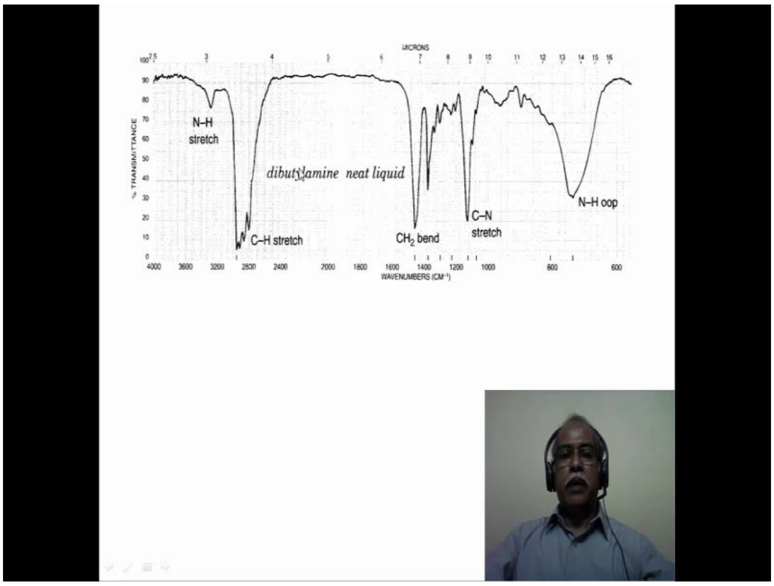

Now, let us go to a dibutyl amine. This is a secondary amine. This is a primary amine so you see a doublet corresponding to the asymmetric stretching and the symmetric stretching of the N-H. In the case of the dibutyl amine, which is secondary amine there is only 1 band that is seen for the N-H stretching frequency. This is a C-H region and this is N-H region. The C-N stretching is appearing as a fairly intense band, you can see the intensity as increased here for the C-N, the intensity for the N-H as decreased which is other way round in the (Refer Time: 15:02) case of the a primary amine in the case.

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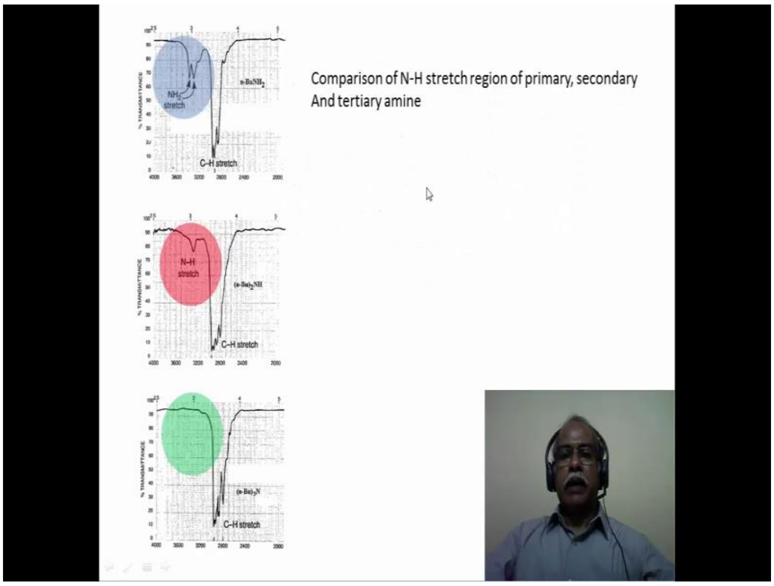

Comparison of N-H stretch region of primary, secondary
And tertiary amine

So, one can compare the N-H region of the primary, secondary and tertiary amine. Tertiary amines do not have any N-H, so you do not see any peak in this region with the blue dotted region for example does not have any contain any peak because there is no N-H in it. This is a tri n butyl amine which is a tertiary amine. This is di n butyl amine and this is butyl amine. So, one can see very clearly in the case of butyl amine doublet, in the case of a di n butylamine a singlet and there is nothing in the case of the tri n butyl amine as in this particular case.

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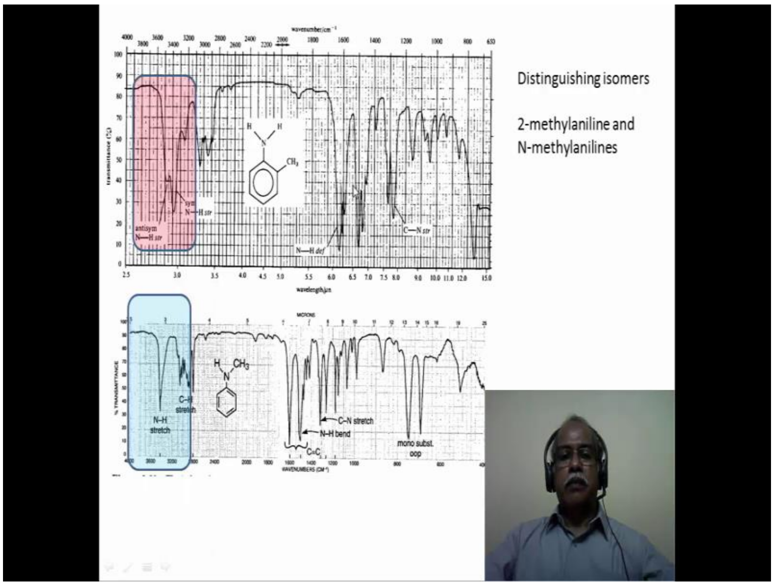

Distinguishing isomers

2-methylaniline and N-methylanilines

This is a distinction between 2 isomers, you have 2 methyl aniline which is the primary amine and N methylaniline which is at secondary amine. Essentially, from the N-H stretching frequency 1 should be able to tell the difference between primary amine and a secondary amine. In the case of the primary amine it appears as a nice doublet in the infrared region of N-H stretching frequency region, whereas in the case of the secondary amine s sharp singlet is what is observed for the N-H stretching frequency. Here, you have the asymmetric stretching and the symmetric stretching of the N-H, whereas here is only 1 type of N-H stretching frequencies what is being observed. In both cases of course, 1 observes the C-N stretching frequency this corresponds to the C-N stretching frequency which is also present in the case of the secondary amine as C-N stretching frequency which corresponds to this particular value here.

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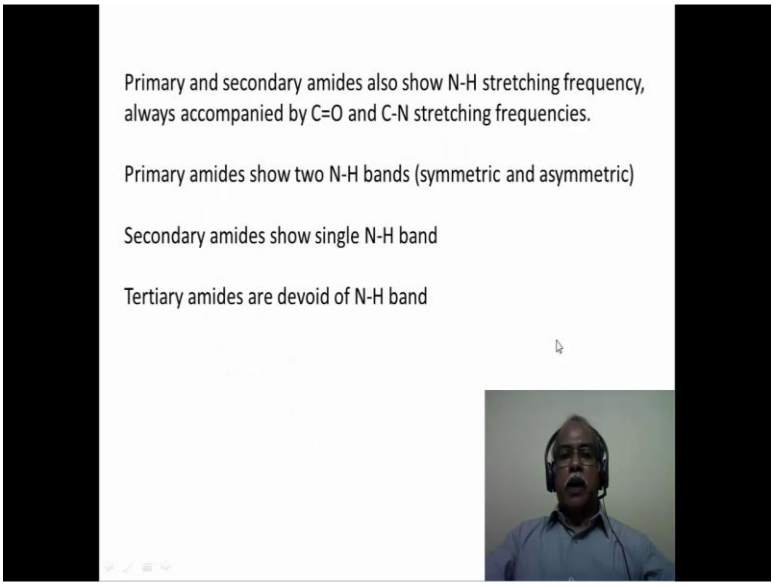

Primary and secondary amides also show N-H stretching frequency, always accompanied by C=O and C-N stretching frequencies.

Primary amides show two N-H bands (symmetric and asymmetric)

Secondary amides show single N-H band

Tertiary amides are devoid of N-H band

In case of amides also one has N-H stretching frequencies but it is always accompanied by C double bond O stretch as well as the C-N stretch the amide functional group has the N-H stretching C-O stretching as well as the C-N stretching. In the case of amine these 2 this band will be missing the carbonyl band will be missing in the case of amines and anilines, but amides do have carbonyls so there will be additional bands because of the carbonyl stretching frequency in the amide. Primary amides as usual show 2 bands symmetric and asymmetric of the N-H stretching frequency. Secondary amide show only one N-H tertiary amides are devoid of the N-H stretching frequency because they do not have any N-H present in this system.

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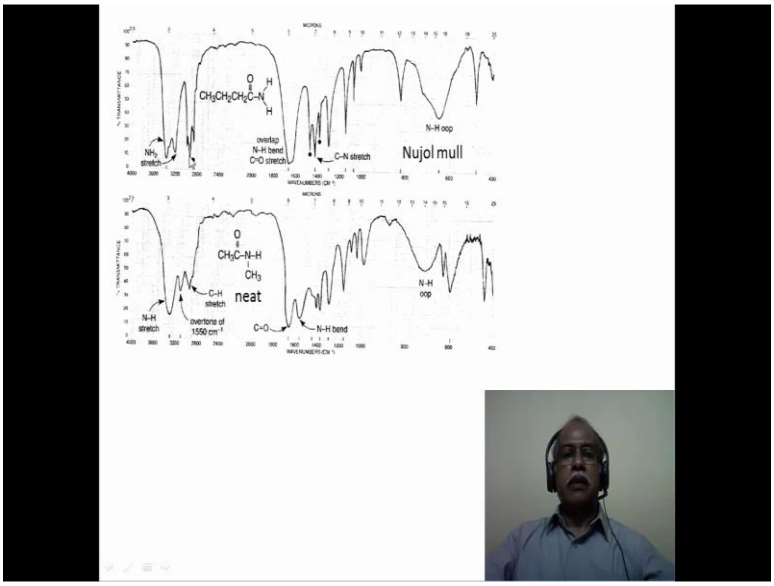

So you can see here this is a butramide, the primary amine. So, one can see the doublet kind of a structure here for the N-H, this is a Nujol peak and this dotted peaks are the nujol peaks for example, this measured as a nujol mull, this is solid sample. Whereas in the case of n methyl acetamide this is a neat sample as a liquid there is a only single band band that is seen for the N-H stretching frequency. In both cases, in addition to the N-H stretching frequency one can also see the carbonyl stretching frequency corresponding to the amide carbonyl of this system which is coming at a value around 1615 or 1617 or so in these 2 cases.

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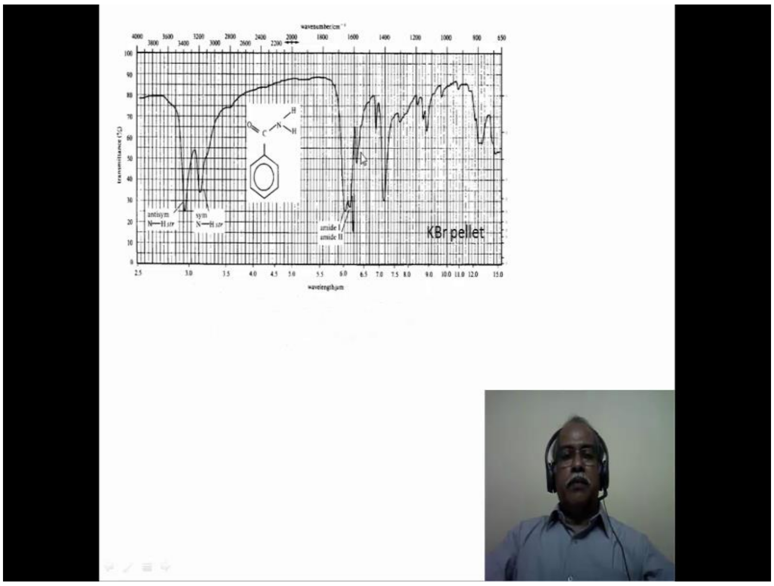

This is Benzamide. Benzamide again has 2 stretching frequencies, this is a primary amide so N-H asymmetric stretching and N-H symmetric stretching is what it is seen in this particular case. In addition to that the carbonyl peaks are also seen in the case of the benzamide as a additional peak. This is measured as a KBr peltet because benzamide is a solid one can measure the KBr spectrum.

So, what we have seen is a very important region where you can distinguish between C-H, O-H and N-H stretching frequencies of various functional groups in which they occur and we will continue in the next module with carbonyl stretching frequencies.

Thank you very much for your attention.