**Application of Spectroscopic Methods in
Molecular Structure Determination
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**Lecture – 27
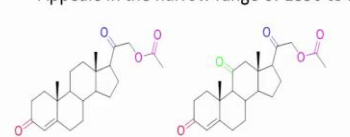Infrared Spectroscopy or Vibrational Spectroscopy**

Hello! Welcome to module 27 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. We have some more portions to cover in the infrared spectroscopy. In this module, we will talk about the important functional groups such as carbonyl functional group, nitro functional group, nitrile functional group and so on.

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Now, carbonyl functional group is a very important functional group. The carbonyl group appears in several different functional groups such as ketones, aldehydes, esters, carboxylic acids, amides and anhydrides. The carbonyl stretching frequency appears as a very intense band in the infrared spectrum that one cannot miss its presence or its absence in the infrared spectrum. The carbonyl stretching frequency appears in a narrow region of 1850 inverse centimeter to about 1600 inverse centimeter. Although it is a fairly narrow region, each one of the carbonyl functional group has its own unique place

in terms of the nature of the carbonyl functional group.

Let us take the example of this particular molecule. It a steroidal skeleton, this is an alpha beta unsaturated ketone. It has a saturated ketone as well as an ester functional group. Now, the functional groups are color coded and the corresponding frequency of the carbonyl stretching frequency is also color coded. For example, the alpha beta unsaturated carbonyl functional group comes at 1660 inverse centimeter whereas, the saturated carbonyl functional group comes around 1735 because it is a ketone. And, when it is in the form of an ester, it comes even at a higher frequency of 1760. So, from the infrared spectrum we get a wealth of information as far as the carbonyl functional group is concerned.

Now, in the right hand side there is a similar structure, except one more carbonyl is added to distinguish between an open chain ketone and a cyclic ketone. This is a cyclic ketone. Cyclic ketone can be distinguished from the open chain ketone by the different frequency that it appears in the infrared spectrum. So, although it looks like a narrow region, the carbonyl functional group is a fairly well defined functional group in terms of the stretching frequency that it comes in the infrared spectrum depending upon what kind of carbonyl functional group we are discussing. Therefore, every type of carbonyl functional group has its unique place in the infrared spectrum.

This is further described here. The base value for the carbonyl stretching frequency in various types of saturated carbonyl functional group is given here. For example, anhydrides have two bands. One is because of the symmetrical stretching the other one is because of the asymmetrical stretching. So, the asymmetrical stretching band comes at 1810 and the symmetrical stretching band comes around 1760. You should take this as a base value. I will tell you what is meant by a base value and how it is affected when conjugation and other phenomena takes place.

Now acid chloride for example, has the value of 1800 inverse centimeter. So, in fact, the anhydride and the acid chlorides are the highest stretching frequency values for the carbonyl stretching frequency, whereas, the amide comes at the lowest stretching frequency value among the carbonyl functional group. The reason is explained as follows.

Let us take the example of either an ester or an acid chloride. Let us take the example of the acid chloride. Now, the carbonyl functional group is connected to an electron withdrawing chlorine atom or a fluorine atom, depending upon the halide that you have in the acid halide. As a result of the inductive effect of the carbon-halogen bond, the electron on the carbonyl carbon gets depleted. This is compensated by the participation

of the lone pair of electrons from the oxygen, which further strengthens the carbonyl bond. Therefore, the bond order of the carbonyl bond in the case of an acid halide or the bond strength or the force constant of the carbonyl bond in the acid halide is much more than, for example, in the case of ester, that is the reason the acid halide comes at a higher frequency compared to the ester.

Now, let us compare the ester and the amide. The ester comes around 1735, whereas the amide comes at a lower frequency of 1690. This is explained as follows. In the case of the ester as well as the amide, the same electro negativity plays a role in terms of the withdrawing nature of the heteroatom namely oxygen and nitrogen in the case of ester and amide, however this is going to be much less pronounced compared to halogen because oxygen and nitrogen are less electro negative than the halogen atom itself.

Now, in the case of oxygen it is sufficiently electro negative to have this effect and thereby increasing the bond strength or the force constant of the carbonyl stretching frequency. So, that comes around 1735. In the case of the amides, there is another factor that needs to be considered; namely the delocalization of the lone pair of electrons from the nitrogen on to the carbonyl functional group, which has the resonance structure here. From the resonance structure, we can tell that the carbonyl carbon oxygen bonds strength or the bond order is decreased. So, as a result of that the stretching frequency also is quite a bit decreased compared to the ester.

So, one has to (Refer Time: 05:27) out these two effects, namely the effect of electron withdrawing by inductive effect and the electron donation by means of a resonance effect. These are the two factors that needs to (Refer Time: 05:34). In the case of amides, this is the overriding factor; namely the delocalization and the resulting canonical structure is an overriding factor. Whereas, in the case of esters and acid chlorides, it is, the overriding factor is a electro negativity and the inductively electron withdrawing nature of the oxygen and the halogen respectively, which pushes the carbonyl stretching frequency of acid chlorides and the ester much higher than the amides itself.

So, this is something consistently you will see in the entire spectroscopy or infrared spectroscopy of carbonyl compounds. The anhydrides come at the highest stretching

frequency value and the amides comes at a lowest stretching frequency values in the infrared spectrum, aldehydes, ketone, esters and so on, they come in between region.

The acid is a very special case because it depends on whether the acid existing as a monomer or hydrogen bonded dimer kind of a structure. In case of a hydrogen bonded dimer kind of a structure, it will come around 1710, whereas in the case of monomeric acid functional group, it should somewhere around close to the ester around 1730 or 1740 in that particular region. We will look into the effect of the hydrogen bonding and other electronic effect in the next few slides.

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The factors that contribute to the carbonyl stretching frequency, first we will consider the electronic effect. Now, we are comparing for example, the force constant dependency on the electron withdrawing nature of the groups that are attached to the carbonyl functional group. We are comparing acetone, trifluoroacetone and hexafluoroacetone.

Now, as we go from acetone to trifluoroacetone, the trifluoro group is electron withdrawing functional group that is going to deplete the electron density on the carbonyl carbon, thereby forcing the carbon oxygen bond to be strengthened by the participation of lone pair of electron from the carbonyl oxygen on to the carbon oxygen

bond. This effect will further increase when you have two trifluoromethyl groups.

In other words, we should have twice the effect of the electron withdrawing effect of the functional group of C F three groups attached to the carbonyl. Therefore, if we look at the bond strength in terms of the carbon oxygen bond strength or the force constant, acetone will have the lowest force constant, whereas hexafluoroacetone will have the highest force constant; which is reflected in the form of the increasing frequency as you go from acetone to trifluoroacetone to hexafluoroacetone.
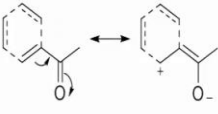
Now if you compare, for example, an acid fluoride with acid chloride, acid chloride in the chlorine is less electro negative than fluorine. So, the carbon fluorine bond is a much more electron withdrawing group, which again strengthens the carbonyl bond by the participation of the oxygen lone pair on to the CO bond in this particular case. And, the chlorine being less electro negative, the force constant in this chloride is going to be much less than the fluoride. So, the acid fluoride also comes at a high frequency compared to acid fluorides. Acid bromides have a very peculiar effect because the mass also increases, which will decrease the stretching frequency and the electro negativity also decreases, which will also decrease a stretching frequency.

So, it could be actually a combination of two effects of mass effect as well as the electronegativity effect, which decreases the carbonyl stretching frequency as you go from carbonyl fluoride to carbonyl chloride to carbonyl bromides.

Effect of conjugation on C=O stretching frequency

Conjugation increases the single bond character of C=C and C=O Bonds in the resonance structure.

$C_8H_{17}CHO$ (sat) 1730 cm^{-1}
Crotonaldehyde (unsat) 1695 cm^{-1}
Benzaldehyde (unsat) 1700 cm^{-1}

lowering of bond order
lowering of force constant
hence lowering of C=O
stretching frequency

Lowered by 25 to 45 cm^{-1}
from the base value

Now, the effect of conjugation on the carbonyl stretching frequency is discussed in this particular slide. Conjugation increases the single bond character. You can see from the resonance structure that is written here and alpha beta unsaturated carbonyl functional group. This carbon-oxygen double bond is no longer a double bond. It becomes a single bond in this canonical structure. So, the actual bond order is less than 2 but more than 1.

If that is the case, this stretching frequency should decrease because the force constant should decrease in the case of the conjugated carbonyl functional group. The conjugation could be because of an isolated double bond in conjugation with carbonyl functional group or it could be because of part of an aromatic system being conjugation with the carbonyl functional group, the lowering of the bond order and the lowering of the force constant, and hence the lowering of the carbonyl stretching frequency is what one would normally observe.

This is illustrated by the examples that are shown here. If we take non-aldehyde which is C nine aldehyde, the stretching frequency of the carbonyl function, we are talking about this C O stretch in all these cases. It comes around 1730 inverse centimeter and crotonaldehyde, which is an alpha beta unsaturated carbonyl functional group comes around 1695. Benzaldehyde, which is also an alpha beta unsaturated system except the

alpha beta unsaturation comes from the phenyl group that is attached to the aldehyde functional group that comes around 1700 inverse centimeter.

So, when we talk about base value, we are actually talking about the saturated compound base value. And, whatever the electronic effect that may be, we add some numbers or subtract some numbers to get the actual values of the alpha beta unsaturated system and so on. In the case of the alpha beta unsaturated carbonyl functional group, the stretching frequency is lowered anywhere from 25 inverse centimeter to 45 inverse centimeter from the base value, which is normally is the value that is given with a carbonyl functional groups of various kind. In this particular chart it is given. This is the base value that we normally talk about.

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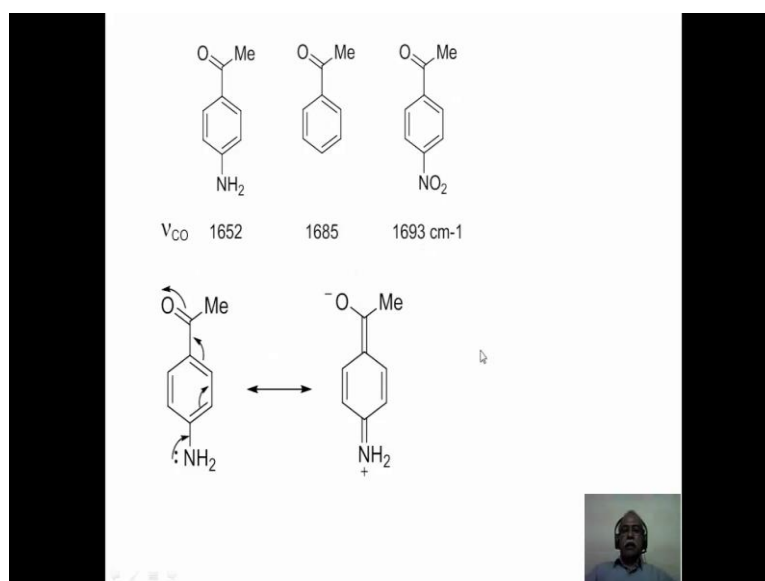
Now, let us consider the example of para amino acetophenone and para nitro acetophenone. The stretching frequency keeps increasing as you go from para amino acetophenone to para nitro acetophenone. Now, if you take acetophenone as the base value for the alpha beta unsaturated carbonyl system, this is correct at 1685. So, from the base value of about 1720 or so, we have decreased it by 40 or 35 inverse centimeter to arrive at the 1685.

Now, what happens when you have an electron donating groups in the para position? This is the kind of resonance effect. The para amino functional group is going to have on carbonyl para amino acetophenone. We can see the canonical structure has the carbon-oxygen single bond and the other canonical structure has the carbon oxygen double bond. So, the bond order essentially gets decreased because of the electron delocalization on to the carbon oxygen bond here. So as a result of that, the stretching frequency also decreases when you go from acetophenone to para amino acetophenone.

Now, when it comes to para nitro acetophenone, the para nitro group is an electron withdrawing group. So, that should essentially decrease or deplete the electron density on this particular carbon and that in turn, should participate. The participation of lone pair of electrons on the oxygen on to carbon oxygen bond should increase the force constant. So, one gradually sees the increase in the stretching frequency of the carbonyl functional group as one goes from the para amino, which is an electron donating group to para nitro which is an electron withdrawing group. The effect of these electronic effects on the carbonyl stretching frequencies is what is illustrated in this slide.

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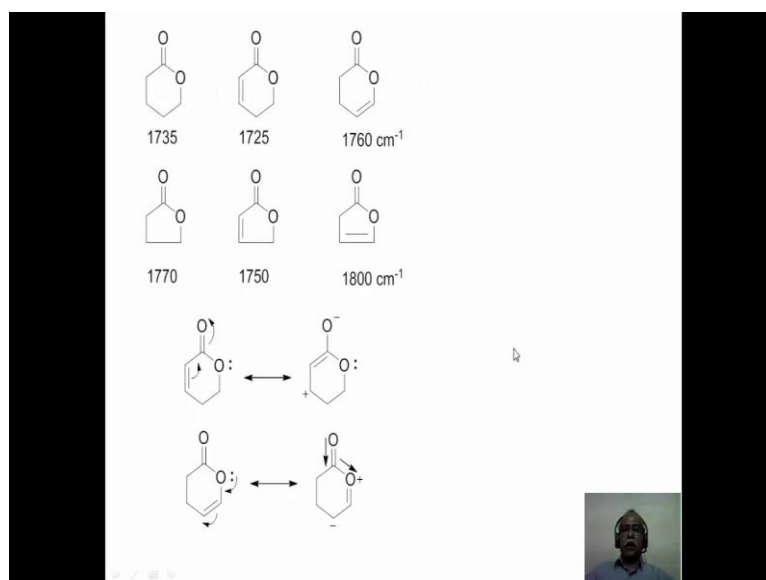
Now, the size of the ring also has a very peculiar effect in terms of the carbonyl stretching frequency. As you go from, sorry, let us first talk about the unsaturation or the

conjugation of the carbonyl functional group. This is this alpha beta gamma, this is delta lactone and this is gamma lactone. In the case of delta lactone, this is a six membered lactone, saturated lactone and it is essentially an ester functional groups. So, 1735 is the base value because this molecule is divided of any kind of strain because it is a six membered ring, it comes around 1735.

Now, what happens when you do an alpha beta unsaturation to this molecule? In other words, this is unsaturated lactone. In this particular case, the value decreases by 10 inverse centimeter to 1725 and when you have the unsaturation closer to the oxygen of the lactone, rather than closer carbonyl. In other words, this unsaturation is in conjugation with the carbonyl, whereas this unsaturation is in conjugation with the oxygen of the lactone. Under these circumstances, when you have an unsaturation along the carbon oxygen carbonyl bond, this delocalization essentially reduces the bond order, and that is why the stretching frequency decreases. Whereas, this unsaturation next to the oxygen essentially allows the participation of the oxygen lone pair to be delocalized on to the vinylic system there, thereby this oxygen actually acquires a positive charge or it becomes electron deficient because of the delocalization; which in turn triggers the mechanism of pulling the electron from the carbonyl function, oxygen to the carbonyl carbon oxygen bond, thereby increasing the force constant of this particular carbonyl with respect to this carbonyl here.

So, an alpha beta unsaturated lactone is reduced by about 10 inverse centimeter from the base value. Whereas, the unsaturation when it is closer to the oxygen participation, lone pair of oxygen, from this particular oxygen participating on the delocalization as it is shown in the bottom resonance structure, the value increases because the force constant of this carbonyl is much higher than the force constant of this particular carbonyl.

We will consider the decrease in the ring size and how it affects the carbonyl stretching frequency in a minute. But, the trend what you have to see here is this is a saturated gamma lactone, this is an alpha beta unsaturated gamma lactone, this is a beta gamma unsaturated lactone, gamma lactone.

So, as you can see from the 1770, it decreases to 1750 and from the 1770, it increases to

1800. For the same reason that we discussed in the case of the delta lactone because of the two effects, namely the delocalization of the double bond on to the carbonyl functional group or the delocalization of the lone pair of electron on to the vinylic system. As opposite affects in terms of the stretching frequency is being reduced in the case of alpha beta unsaturation and stretching frequency being increased, if they have a beta gamma or beta gamma or beta delta, gamma delta kind of unsaturation as the case may be.

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Ring size effect

Six membered rings with carbonyl groups are unstrained and give CO stretch IR band at 1710-1720 cm^{-1}

With decreasing ring size the CO stretching frequency Increases

In order to accommodate small angles, small rings require the use of more "p" character to make C-C bonds. [sp = 180° and sp$_3$ = 109°]

This increases the s character of C=O sigma bond thus Strengthening it. Force constant increases and hence frequency increases

Now, let us go to these effects of the ring size. A six membered ring with a carbonyl functional group is a relatively unstrained ring because six membered ring can accommodate the hybridization angle of 109 in the saturated carbons and 120 in the case of the carbonyl s p 2 carbon, for example. This gives rise to the I R band at around 1710 to 1720 inverse centimeter, which is the base value normally taken for a saturated ketone, particularly of a six membered cyclohexanone kind of a saturated ketone.

With the decrease in ring size, the carbonyl stretching frequency increases for the following reason. In order to accommodate small angles in the small rings that require the use of the p character more and to make the carbon carbon bonds. In other words, the ring carbon carbon bonds will have to acquire a larger contribution from the p orbitals

rather than from the s orbital because as you go from the larger size ring to the smaller sizer ring, the bond angle keeps decreasing.

For example, the bond angle in the six membered ring can be 109, whereas in the five membered ring it will be much smaller. Whereas when you go to the four membered or three membered ring, it is going to be even smaller than the 109 angle. In the case of cyclobutanone kind, butanone kind of a system you have a 90 degree angle. Whereas, you have a cyclopropanone kind of a system, it will have 60 degree angle or so.

So, in order to accommodate the angle, the best way the molecule can cope with the strain is to increase the p character of the carbon carbon bond. As the p character of the carbon carbon bond increases, the s character of carbon oxygen sigma bond increases, and thereby strengthening the carbon oxygen sigma bond in the case of smaller ring system. The force constant increases in the smaller ring system compared to the relatively unstrained six membered ring. A three membered ring will have a much higher s character of the carbon oxygen bond. As a result of the increase in the force constant, the frequency also increases. This is illustrated clearly in the following examples.

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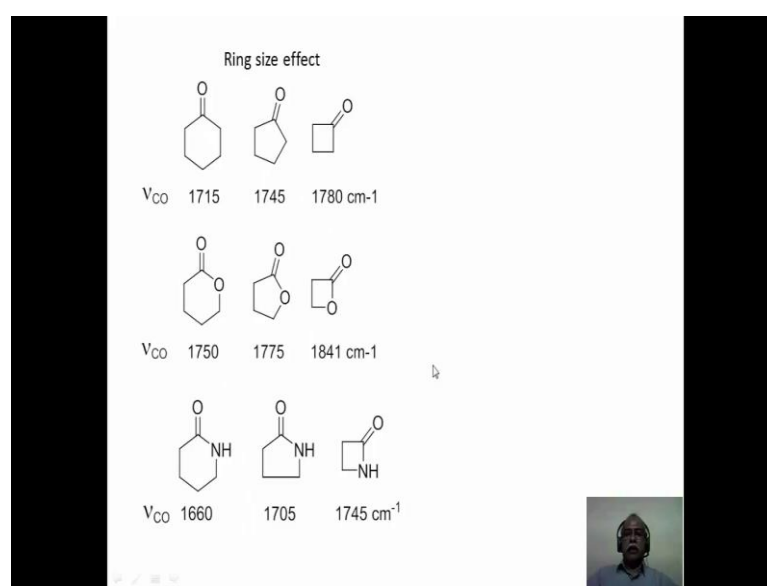
The ring size effect is what is shown here. A saturated six membered is unstrained with a

normal base value of 1715 for the ketone. When it goes to a five membered ring, there is about 30 inverse centimeter increase in the frequency and when it goes to four membered it is about 35 inverse centimeter. So, the four membered and three membered carbonyl groups are the highest value in terms of the carbonyl stretching frequency, among the series of six membered, five membered and four membered.

So when you go from, for example, the ketone to an ester, the frequency should increase. The ester has a higher frequency base value. So, the alpha beta gamma delta lactone has 1750 inverse centimeter. The gamma lactone has 1775 inverse centimeter, whereas the beta lactone has 1845 inverse centimeter.

Now compared to a lactone, the amide should have a lower frequency. That is why it has lower. In case, you can go vertically down or horizontally also. When we go vertically down going from ketone to lactone, increases the frequency; from lactone to amide, it decreases the frequency for the reasons that was discussed earlier. As you go across the row, in each row, the size of the ring decreases from a six membered to a five membered to a four membered, which increases the carbonyl stretching frequency within the series because of the higher strain of the ring and a larger participation of the s electron on the carbon oxygen sigma bond of the carbonyl systems in these cases.

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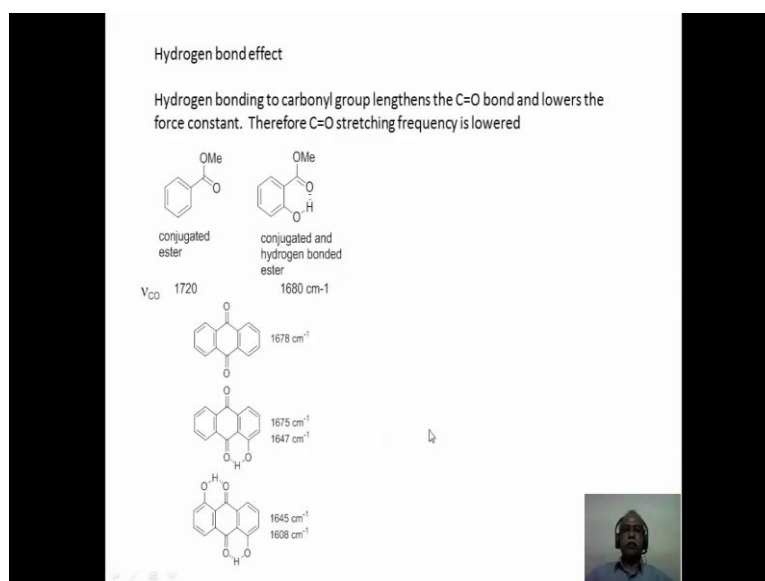
Now the hydrogen bond, usually carbonyl groups, for example in the case of salicyl aldehyde or methyl salicylate kind of orthofunctionalized system, one can have intramolecular hydrogen bond of this type. What happens when a hydrogen bonding takes place to a carbonyl functional group? It essentially lengthens the carbonyl functional group, so carbon oxygen bond, thereby lowering the force constant. Therefore, the carbonyl stretching frequency is lowered because of the hydrogen bonding interaction.

Now if you consider methyl benzoate, this is an alpha beta unsaturated ester. So, compared to the base value for the saturated ester which is about 1740, this is 20 inverse centimeter lower. So, it is 1720 and when it is undergoing a hydrogen bonding interaction with ortho hydroxy derivative. In other words, this is methyl salicylate is what we are referring to because of the intra molecular hydrogen bonding, it is further reduced to 1680. The intramolecular hydrogen bonding effect is beautifully illustrated in the case of the anthraquinones. Anthraquinone with a hydroxyl functional group in the peri position can undergo this kind of a hydrogen bonding interaction.

So, from the base value of 1678 for an alpha beta unsaturated carbonyl functional group in the case of anthraquinone, it reduces to 1647. There are two types of carbonyl groups. One is hydrogen bonded, the other one is non-hydrogen bonded. The non-hydrogen bonded essentially comes in the same region at 1675 like this one here. Whereas hydrogen bonded one is reduced by about 30 inverse centimeter to 1647 or so.

This is a doubly hydrogen bonded system. In this particular case, there are two stretching frequencies which are obtained. One is probably due to the carbon-carbon bond, double bond, the other one is because of the carbonyl stretching frequency which is 1645. So, one can see the hydrogen bonding essentially reduces the carbonyl stretching frequency to lower stretching frequencies in most cases.
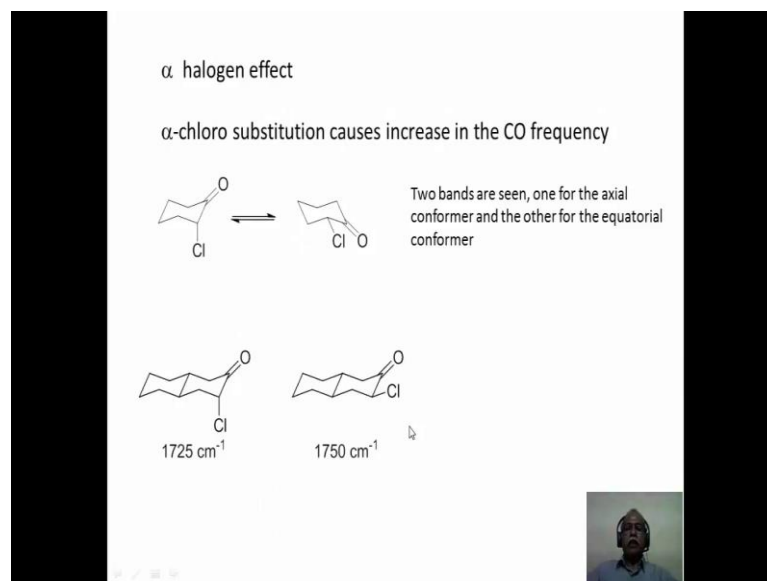
The effects of alpha halogen, there are two effects one can discuss. One is shear electron withdrawing nature of the alpha halogen because of the higher electro negativity, which should push the carbonyl stretching frequency to higher values. In the case of cyclohexanones, you can have either an axial chlorocyclohexanones or an equatorial chlorocyclohexanone. In the case of axial cyclohexanone, it is purely electron inductive effect; is what is felt by the carbonyl functional group, which increases the force constant of the carbonyl functional group, thereby increasing the stretching frequency of the carbonyl functional group of the alpha chloro derivative.

In the case of an equatorial isomer, equatorial conformer for example, the carbon chlorine dipole as well as the carbon oxygen dipole point in the same direction. So, there should be dipolar repulsion. As a result of the dipolar repulsion, the carbon oxygen bond has a higher force constant and as a result of a higher force constant, it will have a higher stretching frequency value. This is clearly illustrated in the case of a rigid system, which does not have this kind of a dynamic process. In other words, two chloro cyclohexanone can exist either in this conformer or in this conformer.

In fact, the infrared spectrum will give you two bands, one corresponding to the axial chloro derivative and the other one corresponding to the equatorial chloro derivative. If

the axial equatorial interconversion, chair to chair interconversion is frozen as in the case of the decalone, then the axial chloro as well as the equatorial chloro or diastereo isomers, and they have independent existence and they can be separated. And, separately they can measure the infrared spectrum. For the axial chloro derivative, it is 1725. It is close to the actual saturated compound which is cyclohexanone comes around 1710 or so. Whereas, the equatorial chlorine derivative because of dipole dipole repulsion that we talked about, it comes at a much higher delta value compared to the axial chloro derivative.

So, one can easily distinguish if two chloro derivatives are available, which one is axial chloro and which one is equatorial chloro, can be easily decided by the carbonyl stretching frequency of the alpha halo derivatives of this kind.

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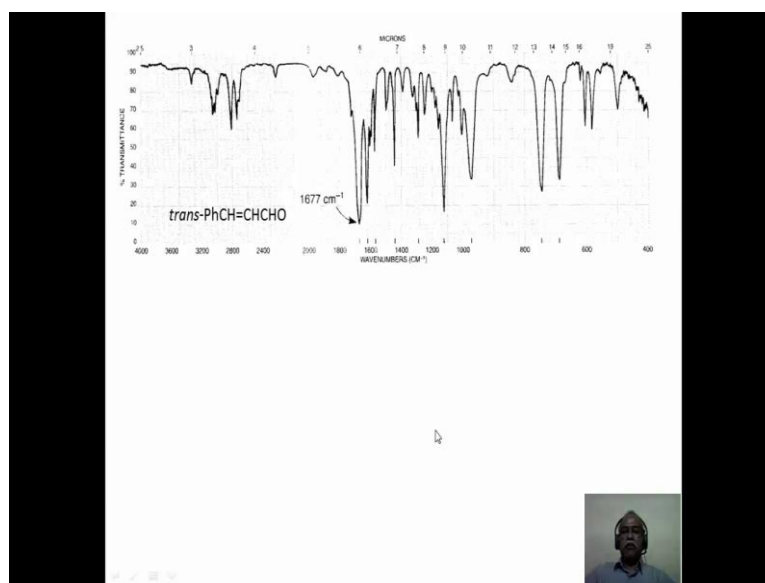
Let us have a look at some representative examples of carbonyl compounds; infrared spectra. This is trans cinnamaldehyde. Trans cinnamaldehyde is an alpha beta unsaturated system. So, one can see the carbonyl stretching frequency at 1677, which is a very sharp and very intense band in this particular case. The CH stretching frequency of the aldehyde functional group, the aldehyde CH usually comes as two lined pattern, somewhere around 28 inverse and 288 inverse centimeter is where it comes. So, you can

see here 2800 inverse centimeter. You see a doublet kind of a thing because of the carbon hydrogen stretching of the aldehyde functional group.

Otherwise, the alpha beta unsaturated C double bond C stretching is coming somewhere around 1600, which is this particular band because it is a mono substituted derivative, the out of plane bending modes come in this particular region and so on. So this region, essentially we do not interpret it very deeply. Most interesting feature in the spectrum is essentially the carbonyl stretching frequency and the aldehyde CH stretching frequencies are the two most interesting ones.

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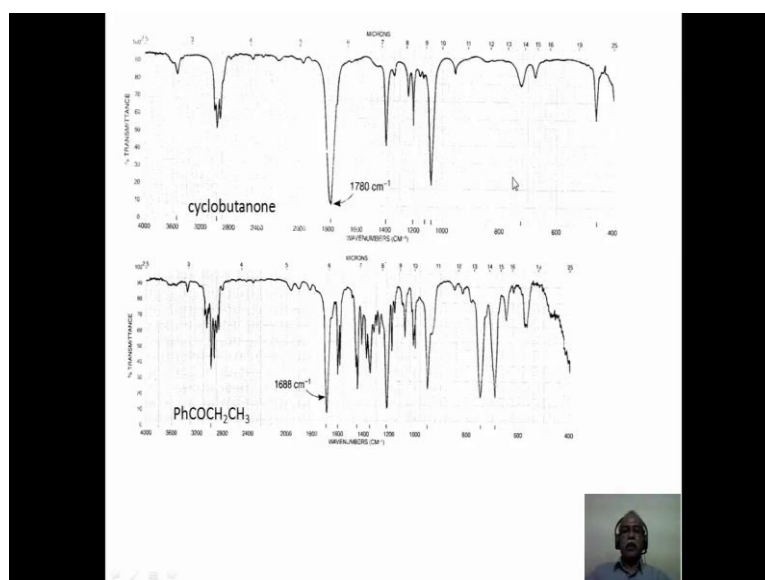
This is cyclobutanone spectrum. Cyclobutanone being a four membered ring system compared to a six membered ring system, which is around 1710 or 1720, it comes at a much higher frequency value 1780 is where it comes. In this particular case, for example and this is again an alpha beta unsaturated system because of the phenyl group. This is propiophenone. Propiophenone has a stretching frequency, carbonyl stretching frequency of 1688 because it is an alpha beta unsaturated compound. Please, see here in the case of cyclobutanone, since there is no C double bonds C unsaturation, you do not see any C double bonds C stretching. This is a relatively free area, whereas in the case of the phenyl derivative, the C double bond C stretching frequency is essentially appears in this

particular region between 1600 and 1500. So, one can also see the out of plane bending of the mono substitutor aromatic system, which is coming in the region of 1702, about 1800 or so in this particular region.

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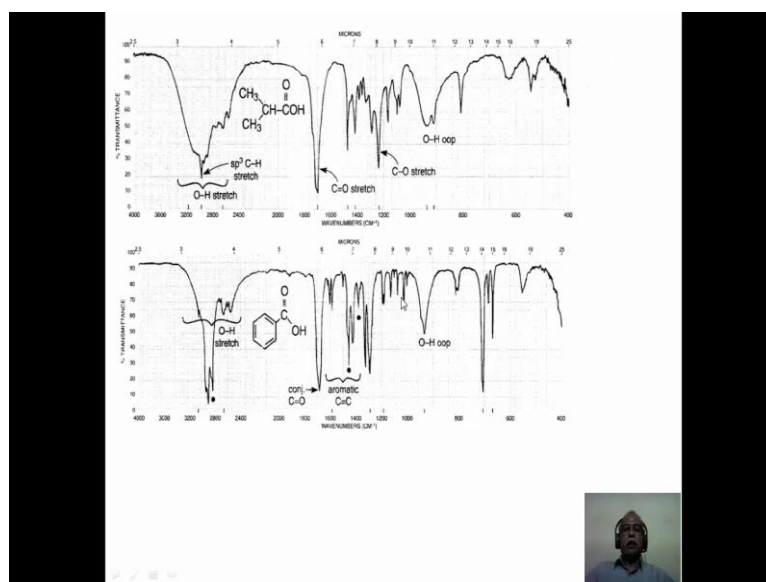
Now, this is an isobutyric acid. In isobutyric acid, there are two unique features one has to observe. One is the carbonyl stretching frequency, which is coming around 1720 or so, in this particular case and that is a very intense band, in this case. It also should have two other recognizable bands, one because of the OH stretch. You can see here, a very broad stretching frequency in the region of 2800 to 3200 inverse centimeter; which is a this big envelop that you see here is essentially because of OH stretching frequency.

Carboxylic acids typically have very broad OH stretching frequency because of intra molecular as well as inter molecular hydrogen bonding interaction. The other feature one can see in the carboxylic acid spectrum is the CO single bond stretching frequency, which comes in this particular case around 1200 inverse centimeter or so. This is for benzoic acid. In addition to the carbonyl stretching frequency, you do see the C double C aromatic stretching frequencies also plus the OH stretching frequency in the usual region in the higher frequency region is very clearly seen.
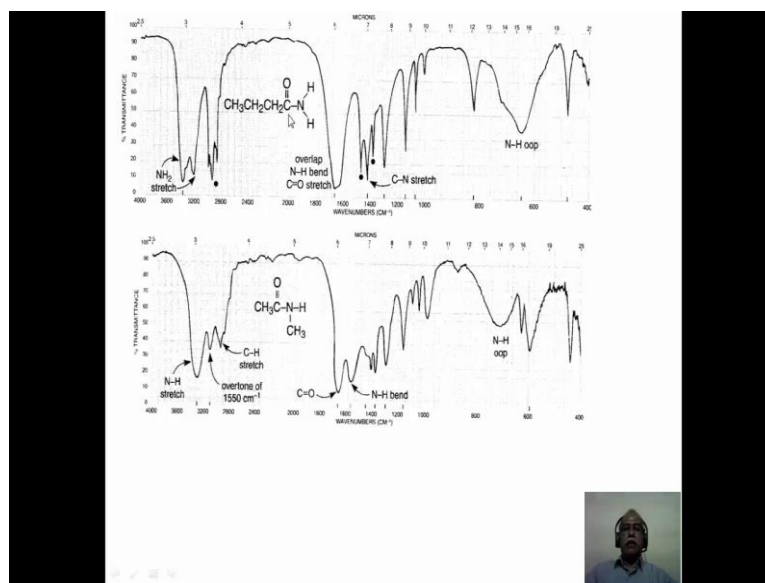
This is a spectrum of a primary amide. This is butyramide. Butyramide spectrum should have the carbonyl stretching frequency coming in this region. Now, one has to discuss the amide a little more detail. The NH bending mode also comes in the same region, around 1660 or 1640 or so and anywhere between 1600 to 1640, the NH bending can also come. So, the amides usually show two bands in the case of the carbonyl region. In the carbonyl region, one because of the actual carbonyl stretching frequency the other one because of the NH bending kind of a mode of frequency. This is called amide one band and this is called amide two band. That is how they are described in the literature. The two bands can be merged as in this particular case, for example. There is an overlap because of the broadening of the signal; one can tell that there is a overlapping of the NH and the CO bond.

Now, the amide functional group also has the NH stretching, if it is a primary amide. We have seen earlier that it should come as a doublet. In fact, it does come as a doublet, whereas if it is a secondary amide as in this particular case, n-methyl acetamide for example, it comes as a fairly broad single line pattern is what one sees for the amide functional group NH stretching frequency as well as the carbonyl stretching frequency.
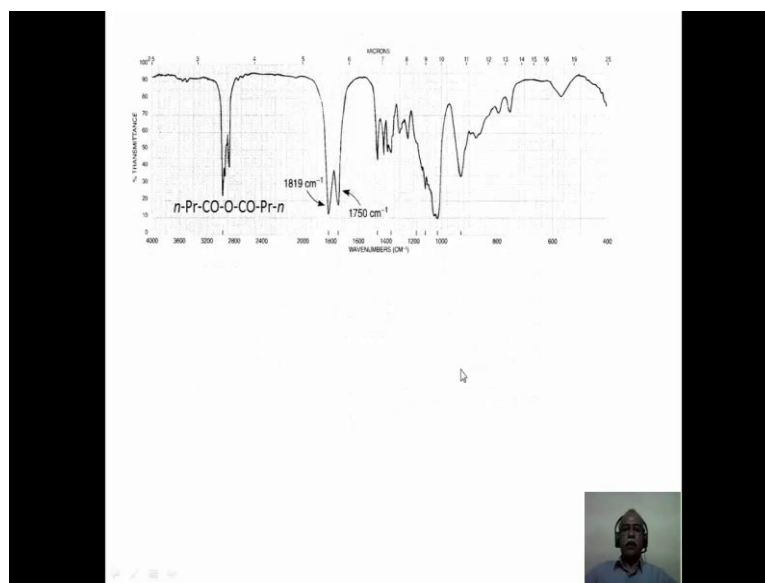
This is a spectrum of a butyric acid anhydride. Butyric acid anhydride, for example, is very clearly does not have the OH functional group, so that region is fairly clean. Only CH stretching frequencies are observed in this region. So, compared to the butyric acid, this is a very different spectrum. So, when you take butyric acid and convert it in to a butyric anhydride, it is easy to follow the reaction by an IR spectroscopy because the OH should disappear completely, once the anhydride is completely formed.

Now, anhydrides also have two frequencies. One because of the asymmetric stretching, the other one is because of the symmetric stretching of the carbonyl functional group, which we have seen earlier. So, the butyric anhydride also shows two bands. The highest band is 1819, which is a symmetric stretch and the lower band is 1750, which is a symmetrical stretch. This is a carbon oxygen single bond stretch is what is seen around one thousand inverse centimeter, in this particular case. So, what we have seen is a wide variety of carbonyl functional group.
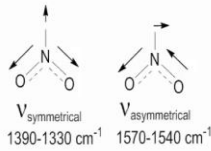
The various factors which affect the carbonyl stretching frequency is what, we have seen in the past few slides. Now, let us look into another important functional group namely nitro functional group. There are two bands that are usually seen for the nitro functional group, also in the region for the N double band O stretching frequency. The N double bond O stretching frequency due to the symmetric as well as the asymmetric stretching of the N double bond O, which is represented pictorially below here for the nitro functional group.

The bands are usually intense because there is a large change in the dipole moment during the stretching and compressing motion of the C, the N double bond O for example and as usual conjugation reduces a frequency by about 20 inverse centimeter. In other words, aromatic versus aliphatic nitro compounds, if we compare the aromatic nitro compounds will have about 15 to 20 inverse centimeter lower stretching frequency for the NO bond compared to an aliphatic nitro compound.
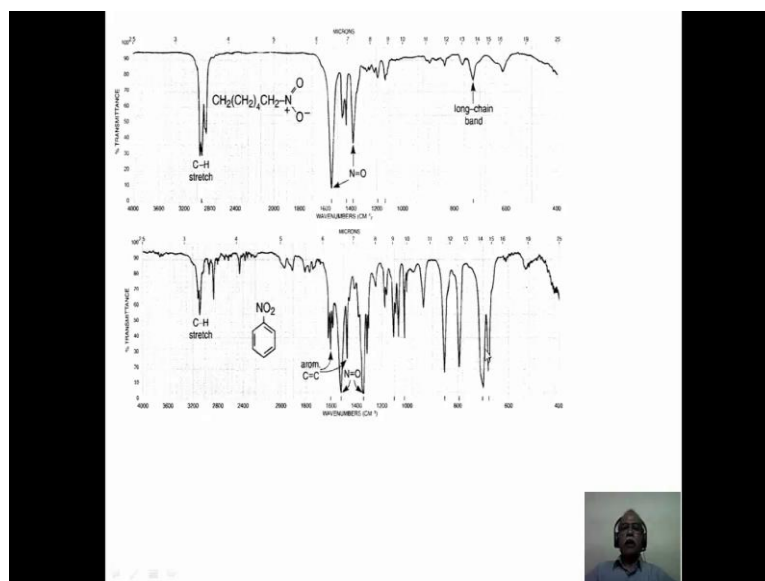
This is a spectrum of a saturated long chain alkyl. This is a hexyl nitro hexane, for example, in this particular case. So, one sees the CH stretching because there are large number of CH bonds in this particular molecule. So, CH stretching in the saturated C H, s p 3 CH stretching is what is seen around 3000 inverse centimeter or so and there are two intense bands in this region between 1500 and from 1500 to about 1300. Whether, carbonyl stretching frequency I forgot to mention the symmetrical stretching frequency can come in anywhere between 1390 to 1330. The asymmetrical stretching frequency can come anywhere between 1570 to 1540.

In fact, it is easy to remember, 1535 and 1350 are the numbers which are the base values one can take as for the nitro compounds. In this particular case, 1530 and this case 1350. The two digits are simply inversed in the case of the two frequencies of the symmetric and the asymmetric stretching frequency of the nitro. So, a saturated nitro compound has a stretching frequency coming around 1560 or so in this particular case and another frequency almost close to 1400 is where it is seen. These are the asymmetric stretching and this is symmetric stretching of the N double bond O.

And when we have the alpha beta unsaturated system, as we can see here, this comes around 1530 or so. Much lower than the value for the saturated nitro compound. You

have again two bands, in addition to that because of the alpha beta unsaturated C double bonds, C one can also C the C double bond C stretching of the aromatic system in this particular region. So, this region now becomes fairly crowded because of the multiple stretching frequencies, which are appearing in this particular region. This is as usual the mono substituted out of plane bending mode of the aromatic system that we are seeing here.

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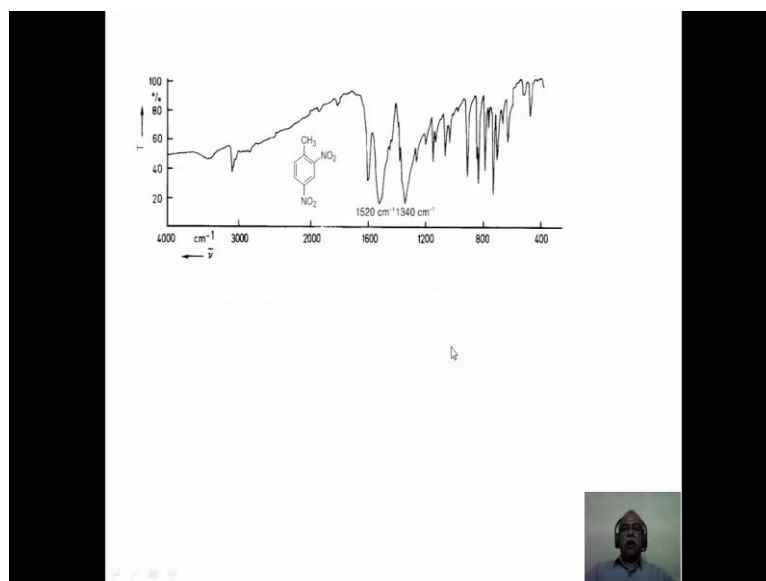
This is two 4 dinitrotoluene. Two 4 dinitrotoluene again has two bands because it is an alpha beta unsaturated system. It is 1520 and 1340 are the two bands corresponding to the nitro functional group in this particular molecule.

The other important functional group is the cyano or the nitrile functional group. The cyano or nitrile functional group typically comes in the region of 2280, 2240 as a single band it will come. Typically, it will come around 2250. You can take this as a base value for the saturated nitrile. It is an intense to medium intensity band. It is not very intense in nature. Compared to carbonyl or compared to nitro functional group, this is not as intense usually, but nevertheless it is an unmistakable region where it comes. So, it should be possible to identify the cyano functional group from infrared spectrum.

As usual, the alpha beta unsaturated nitriles will have a lower frequency compared to saturated nitrile system and cumulenes such as azide, for example, or isocyanate and isothiocyanate, they also come typically in the region between 2200 to 2100 at various stage at various frequencies it comes, one should be able to identify. These are less common functional group as far as organic chemists are concerned. Azide may be a common functional group but isocyanate and thiocyanate, thioisocyanates are not as common as the cyano functional group or the azide functional group in organic chemistry.
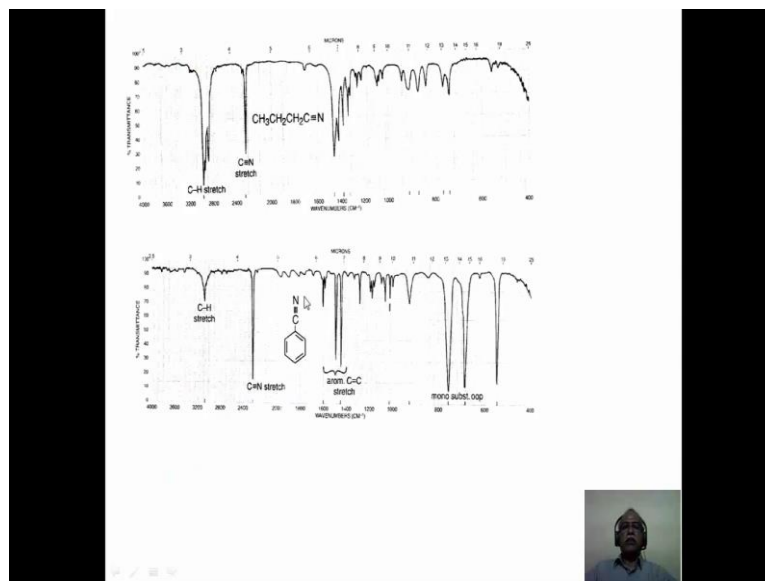
The nitrile, there are two examples given here. Butyronitrile and benzonitrile are the two compounds that is given here. This intense band that one sees around 2200 something frequency is because of the cyano stretching frequency. The C triple bond N stretching frequency actually comes at a lower frequency than a C triple bond C stretching frequency, sorry, the C triple bond C stretching frequency comes at a lower stretching frequency compared to C triple bond N stretching frequency because nitrogen is a heavier element in this particular case. The only difference is the C triple bond C. Sometime one can miss it, if it is internal acetylene because there would not be any dipole moment change. So, the intensity of the C triple bond C is usually weak compared to a C triple bond N kind of a stretching frequency.

In the case of alpha beta unsaturated system, in addition to the C triple bond N, one also see the C double bond C stretching frequency in the normal region of 1600 to 1400 inverse centimeter. This is a mono substituted out of plane mode, out of plane bending mode of the mono substituted aromatic system which is seen as the doublet, usually in this region.
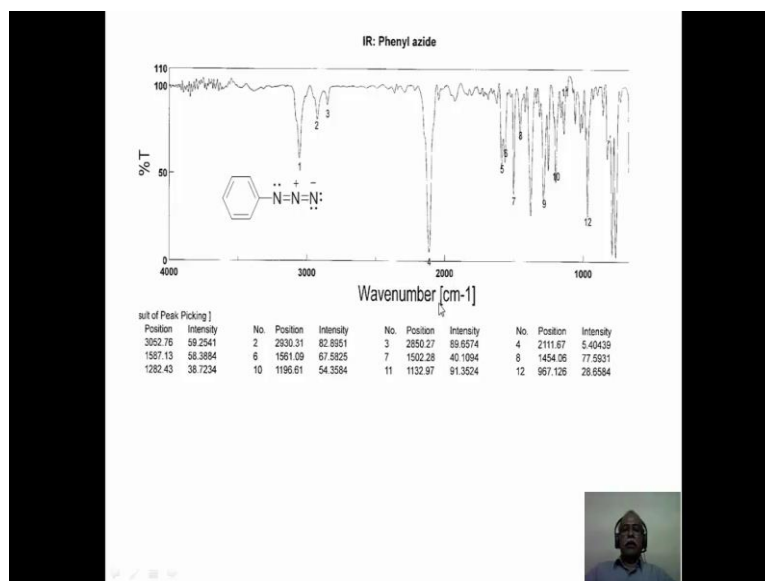
This is an azide. This is phenyl azide. Phenyl azide has a very intense band around 2111. This particular band here is because of the N double bond N stretching frequency. This is actually a cumulene kind of a system. Cumulenes also come in this region of cyano and acetylene kind of a region is where the cumulene also comes. So, this is azide peak N double bond N stretching frequency is what is seen as a cumulene system around 2111, in this particular case.

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So, what we have seen in this module is the important functional group, particularly carbonyl functional group. The various factors that affect the carbonyl stretching frequency and we have seen why the variations take place within the carbonyl stretching frequency, if you are going from anhydride, all the way to amide, how the frequency is affected by the electronic factors. Then, we saw some examples of nitrile and nitro functional group and one example of an azide functional group was also seen.

Thank you very much for your attention.