Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 25

Infrared Spectroscopy or Vibrational Spectroscopy

Hello, welcome to module 25 of the course on Application of Spectroscopic Methods in Molecular Structure Determination. In this module, we will consider infrared spectroscopy and continue with infrared spectroscopy for a few more modules. Like any other spectroscopic method, infrared spectroscopy has its own special place in structure elucidation problem. And, in the hands of organic chemists it is a very powerful tool for identification of functional groups.

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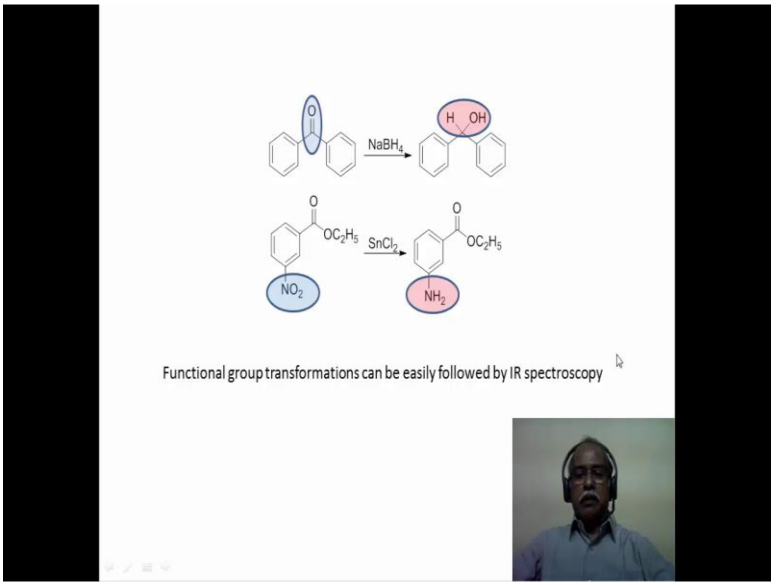

Functional group transformations can be easily followed by IR spectroscopy

Let us consider the following two reactions that are described in the slide. The first reaction is reduction of a carbonyl functional group to an alcohol, in other words, a ketone to an alcohol. The second transformation is a reduction of nitro functional group to amino functional group. If you look at these two reactions, they are essentially functional group transformation. One functional group is getting transformed into another functional group. And, the molecular skeleton itself has very minimal change or no change at all, in terms of the overall molecular skeleton of these two compounds.

So, what is the best way to follow this reaction? If one were to follow this reaction, one can always say I can follow this reaction by NMR spectroscopy or mass spectrometry. But, both these spectroscopic techniques will be overkilled in order to study such simple transformation.

The most widely used spectroscopic techniques for following functional group transformation is infrared spectroscopy or vibrational spectroscopy. So, vibrational spectroscopy has its own special place in molecular structure determination and structure elucidation problems. Functional group transformations can be easily followed by infrared spectroscopy. In fact, infrared spectroscopy is one of the most easily accessible spectroscopic methods in any laboratory. Infrared spectrometers compared to NMR and mass spectrometer is relatively cheaper. And, it is possible to afford the infrared spectrometer much more easily compared to the other two spectrometers namely N M R and mass spectrometer.

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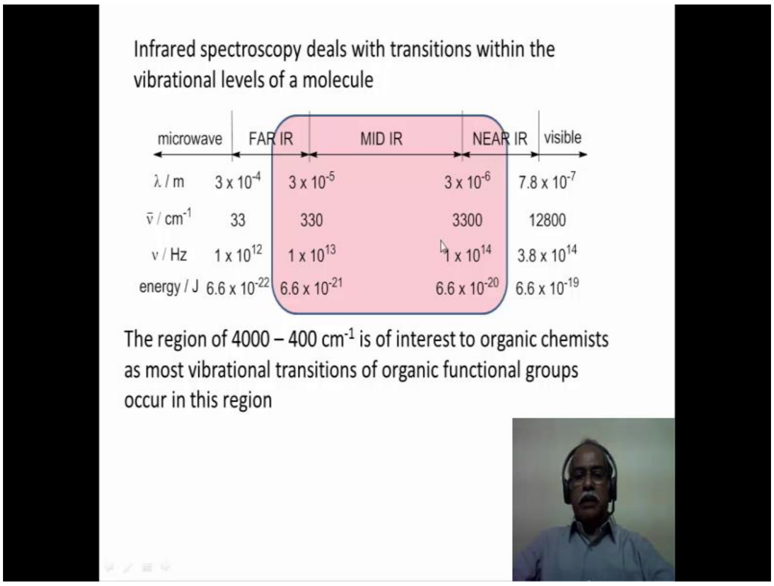

Infrared spectroscopy deals with transitions within the vibrational levels of a molecule

λ / m	3 x 10^{-4}	3 x 10^{-5}	3 x 10^{-6}	7.8 x 10^{-7}
$\bar{\nu}$ / cm^{-1}	33	330	3300	12800
ν / Hz	1 x 10^{12}	1 x 10^{13}	1 x 10^{14}	3.8 x 10^{14}
energy / J	6.6 x 10^{-22}	6.6 x 10^{-21}	6.6 x 10^{-20}	6.6 x 10^{-19}

The region of 4000 – 400 cm^{-1} is of interest to organic chemists as most vibrational transitions of organic functional groups occur in this region

Before we go in to the structure elucidation problem, let us look into some fundamental aspects of infrared spectroscopy. Infrared spectroscopy essentially deals with the transitions within the vibrational levels of a molecule. Molecules have different electronic levels starting from the ground electronic level to the higher excited electronic level. Within the ground electronic level, there are several vibrational level; starting with zero vibrational level, vibrational level 1, 2, 3 and so on. And, the transitions that occurs within the grounds, electronic state vibrational levels of a molecule is what infrared spectrum is all about.

Now, the infrared region is sandwiched between the visible region and the microwave region. Typically, the infrared region is divided into three portions; the far infrared region. In terms of the wave numbers, this is roughly 33 inverse centimeter to 330 inverse centimeter. Then, the mid IR region which is about 332 about 3300 inverse centimeter and then the near infrared region corresponding to 3300 to 12800 inverse centimeter or so. Beyond this, it will be the visible region and beyond this side on the left hand side, it will be the microwave region. In fact, it is the region between 4000 to 400 inverse centimeter. That is of special interest to the organic chemists as most of the vibrational transitions of organic functional group occur in this particular region.

In terms of the energy per photon if you look at, this is a very low energy radiation 6.6 into 10 to the power minus 21, 6.6 into 10 to the power minus 20 joules is the energy per photon of this kind of infrared radiation. Traditionally, infrared spectroscopy is; the energy scale is plotted as wavenumbers, instead of frequencies or as wavelengths, for example. Now, the highlighted region is of the special interest region for the organic chemists calling between 4000 inverse centimeter to 400 inverse centimeter. And, typically all the functional groups can be detected in this particular region.

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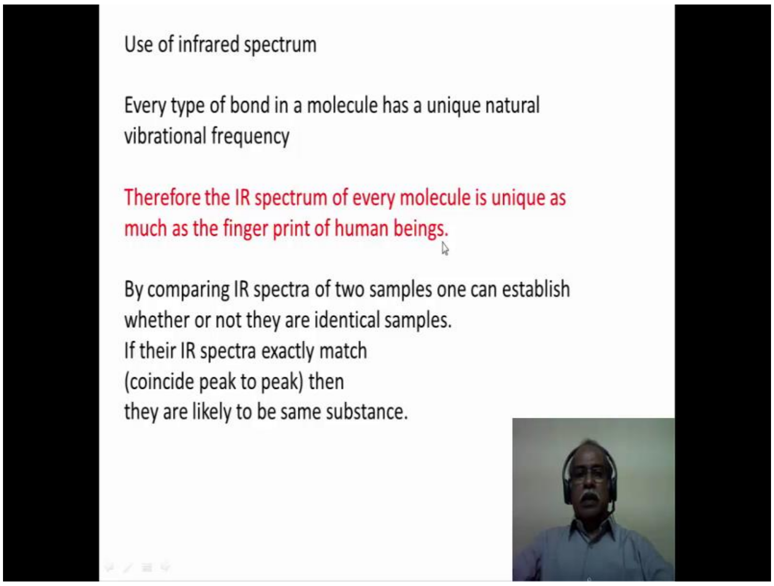

Use of infrared spectrum

Every type of bond in a molecule has a unique natural vibrational frequency

Therefore the IR spectrum of every molecule is unique as much as the finger print of human beings.

By comparing IR spectra of two samples one can establish whether or not they are identical samples.
If their IR spectra exactly match
(coincide peak to peak) then
they are likely to be same substance.

Let us look at the use of infrared spectrum. Every type of bond in a molecule has a very unique natural vibrational frequency. Therefore, infrared spectrum of every molecule will be very unique just as much as the fingerprint of human beings. And, this is what makes the infrared spectroscopy a very valuable tool.

By comparing the infrared spectra of two samples, one can establish whether they are identical samples are not identical samples very easily. If the infrared spectra of these two samples exactly match, in other words, peak to peak matching is happening, then the two substances are likely to be the same. In other words, it is like matching the fingerprint of human beings to identify human beings. One can match the fingerprint regions of the infrared spectrum of two samples. And, if they match exactly on top of each other and then we can consider these two samples to be identical samples.

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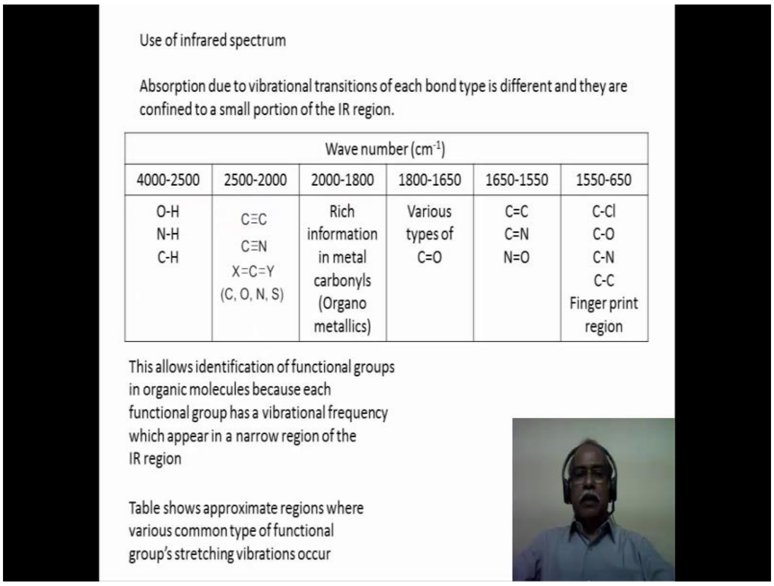

Use of infrared spectrum

Absorption due to vibrational transitions of each bond type is different and they are confined to a small portion of the IR region.

Wave number (cm^{-1})					
4000-2500	2500-2000	2000-1800	1800-1650	1650-1550	1550-650
O-H N-H C-H	$C\equiv C$ $C\equiv N$ X=C=Y (C, O, N, S)	Rich information in metal carbonyls (Organo metallics)	Various types of C=O	C=C C=N N=O	C-Cl C-O C-N C-C Finger print region

This allows identification of functional groups in organic molecules because each functional group has a vibrational frequency which appear in a narrow region of the IR region

Table shows approximate regions where various common type of functional group's stretching vibrations occur

The other use of infrared spectrum, of course is the conventional and traditional use where the vibrational stretching frequencies of various functional groups could be detected in the infrared spectrometer. The absorption is due to the vibrational transition of each type of bond is different. And, they are confined to a very small portion of the infrared region. In fact, the infrared region can be divided into six portions as it is shown here; starting from 4000 to 2500, that is the first region. In this particular region, one can observe the stretching frequency is of OH, NH and CH type of functional group. In other words, the alcohol, amines and hydrocarbons can be detected in this particular wave number region. From 2500 to 2000, triple bonded systems and cumulene systems of this kind can be detected. In other words, C triple bond C stretching, C triple bond n stretching or in case of the cumulene kind of a double bond, one can have allyl isocyanide and thiocyanate kind of a systems, we can have in terms of the functional group detections that one can make in this.

The region between 2000 to 1800 is actually blank as far as the organic chemists are concerned. But, rich information is available when you are dealing with metal carbonyls as an organometallic compounds, for example. Transition metal carbonyls are very visible in this particular region because of the carbonyl stretching frequency, where the carbonyl is attached to a metal atom or metal ion, for example. So, this region essentially for organic chemists, it is not very useful. But, for inorganic chemistry and the organometallic chemists, this region is extremely valuable and gives rich information about the carbonyl stretching frequencies of various types in this region.

Now, from the organic chemistry perspective point of view, this 1800 to 1650 is a very valuable region. In this region, all types of carbonyl stretching frequency occurs; starting from aldehydes, ketones, esters, amide, acid anhydride, acid halides. All of them can be fitted into this narrow region. Although they can all be fitted into the narrow region, where within this region one can divide the region into various section. And, each one of the functional group essentially appears in a different region within this narrow region.

Now, 1650 to 1550 is the double bonded region, where C double bond C, C double bond N, N double bond O kind of functional group can be olefinic or amino functional group or nitroso functional, nitro functional group can be detected in this particular region. The region between 1550 and 650 is actually the fingerprint region. One does not analyze this region in a very detailed manner, except look for some familiar stretching frequencies like the CCl, CO and CN kind of stretching frequency. One does not look for CC stretching frequency in this region because invariably organic compounds are going to have CC stretching frequencies. And, it is probably too complicated to analyze this region for a CC stretching frequency.

So, these six regions allows one to identify functional groups in an organic molecule because each functional group has a vibrational frequency which appears in the narrow region of the infrared spectrum. This table essentially shows the approximate regions, where the various types of organic functional group stretching vibrations occur at different locations, in terms of the various regions that are identified here.

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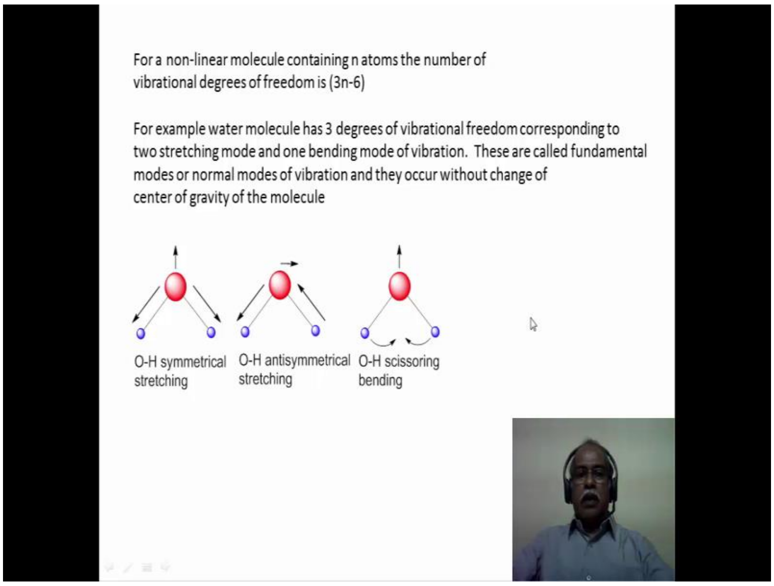

For a non-linear molecule containing n atoms the number of vibrational degrees of freedom is (3n-6)

For example water molecule has 3 degrees of vibrational freedom corresponding to two stretching mode and one bending mode of vibration. These are called fundamental modes or normal modes of vibration and they occur without change of center of gravity of the molecule

Now, let us have a look into the different types of modes of vibration in a molecule. We can consider simple molecules like the triatomic molecule with a linear geometry as well as a bent geometry. In a non-linear geometry, which contains n number of atoms in itself, the number of vibrational degrees of freedom will be 3 n minus 6. In fact, three n will be the degrees of freedom of which three translational freedoms and three rotational freedoms are subtracted. The remaining portion is the vibrational freedom of the molecule having n number of atoms in a non-linear system. For example, if we consider water molecule, it is a bent structure. It is not a linear structure. It has three degrees of vibrational freedom corresponding to the two stretching frequencies which are shown here and one bending mode which is also shown here.

If we consider these two stretching modes, this is a symmetrical stretching of OH bond. In other words, this is called symmetrical stretching of the OH, in terms of the stretching frequency that one can observe for the water molecule. This, here in the symmetrical stretching both the bonds namely the OH bonds are either elongated or compressed simultaneously and in order to maintain the center of gravity. The oxygen also moves and displaces itself from this position, so that the center of gravity remains same in all of these normal modes of vibration.

In the OH, antisymmetrical or asymmetrical stretching, it is called actually asymmetrical stretching. One of the bond, OH bond is elongated. Simultaneously, the other bond is compressed as it is shown. And, in order to again maintain the center of gravity in the same place, the oxygen atoms move in this direction. And, these are the two stretching frequencies.

This is also a stretching frequency, except it is called a scissoring bending mode of vibration in terms of the molecular motions that are involved. If we now consider a scissoring motion of the two OH vibrating in this direction, simultaneously they both come together and move further away in terms of the scissoring action that it has. And, at the same time the oxygen also vibrates in this motion to maintain the center of gravity. That is called the scissoring motion. So, you have the three degrees of vibrational freedom that are represented by three normal modes of vibration in a water molecule.

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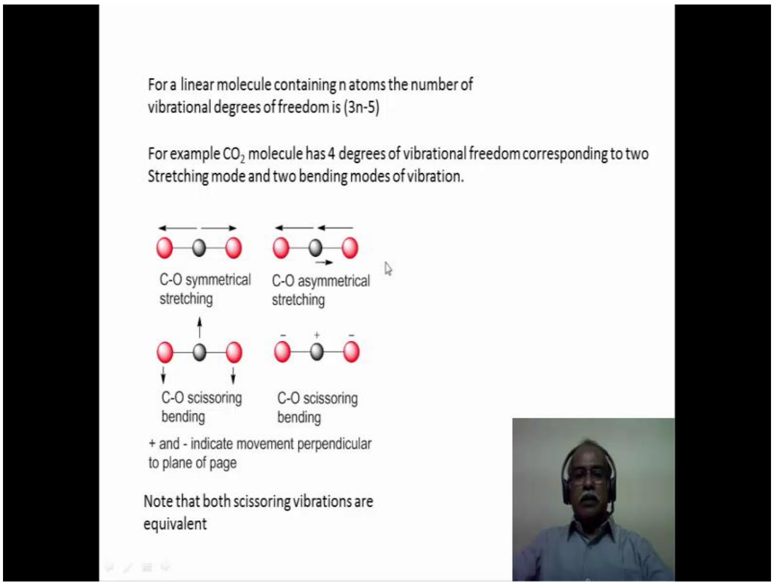

For a linear molecule containing n atoms the number of vibrational degrees of freedom is (3n-5)

For example CO_2 molecule has 4 degrees of vibrational freedom corresponding to two Stretching mode and two bending modes of vibration.

+ and - indicate movement perpendicular to plane of page

Note that both scissoring vibrations are equivalent

And, on the other hand if you consider a linear molecule, the linear molecule will have a freedom, vibrational degrees of vibrational only; 3 n minus 1. For example, CO two has four degrees of vibrational freedom corresponding to two stretching mode and two bending modes, which are shown here.

In the CO stretching mode, you can have the carbon and the oxygen bond stretched out or pushed in. In other words, they are either simultaneously compressed or simultaneously they are stretched out. And, this is called the symmetrical stretching of the carbondioxide. In the asymmetrical stretching of carbon dioxide, one of the bond is compressed. And, simultaneously the other bond is elongated. In order to again maintain the center of gravity, the oxygen, the carbon atom moves towards this direction as it is shown.

Now, there are two scissoring or bending modes of vibration in the carbondioxide. If we consider on the plane, the bending of these two oxygens and making a non-linear geometry in the process with a simultaneous motion of the carbon upwards and the two oxygen downwards, this will be one particular scissoring or bending modes of vibration.

If you consider this is within the plane of the paper. Suppose, if we consider above and below of the plane of the paper motions, in other words, the two oxygen go below the plane of the paper and the one oxygen coming above the plane of the paper. This is also another scissoring mode. Both these vibrations are equivalent vibrations, except they occur in two different planes. So, these are the four degrees of vibrational freedom or the normal modes of vibration for a molecule like carbon dioxide.

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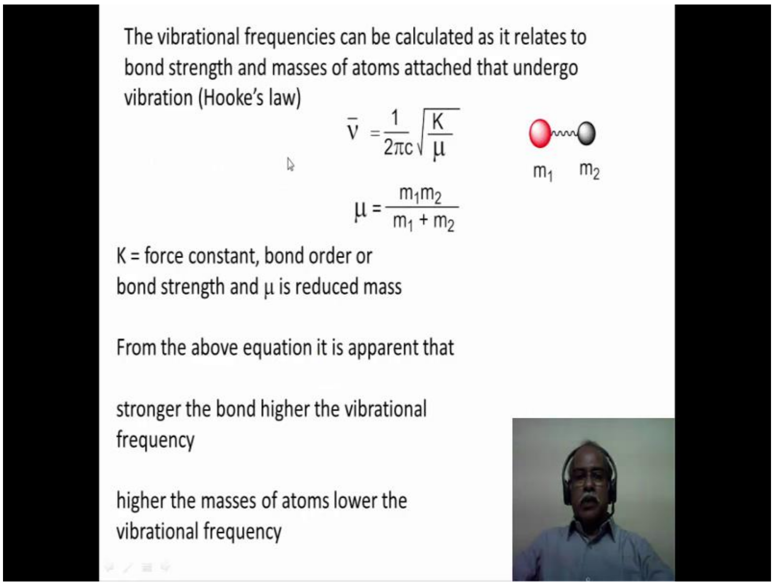

The vibrational frequencies can be calculated as it relates to bond strength and masses of atoms attached that undergo vibration (Hooke's law)

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

K = force constant, bond order or bond strength and μ is reduced mass

From the above equation it is apparent that

stronger the bond higher the vibrational frequency

higher the masses of atoms lower the vibrational frequency

Now, how does one calculate the vibrational frequencies, which are related to bond strength as well as masses at atom that are connected to the bond? Let us consider two atoms connected by a bond which is represented by a spring as an example, as an illustrative example for (Refer Time: 12:30).

How do we calculate the vibrational frequency of these two atoms stretching and compressing itself, during the course of the vibration? This is done using Hooke's law. Hooke's law relates the frequency or the wave number of vibration corresponding to two parameters. It is directly proportional to the square root of K; where K is a force constant which can be in all practical (Refer Time: 12:57) considered as bond order or bond strength and mu which is the reduced mass, essentially corresponding to the two masses m 1 and m 2. If they are connected together, then mu is equal to m 1 m 2 divided by m 1 plus m 2. And from the above equation, it is apparent that the stronger the bond strength it is, the vibrational frequency will be higher. In other words, this is directly related. K and mu are directly related to each other. Whereas higher the mass, lower will be the frequency; because mass is inversely proportional to the; reduced mass is inversely proportional to the wave number or the frequency of the vibration.

So, these are the two important parameters namely the force constant, which is related to bond order or bond strength. And, the reduced mass which is related to the masses that are connected to the bond that we are considering for the stretching motion purposes.

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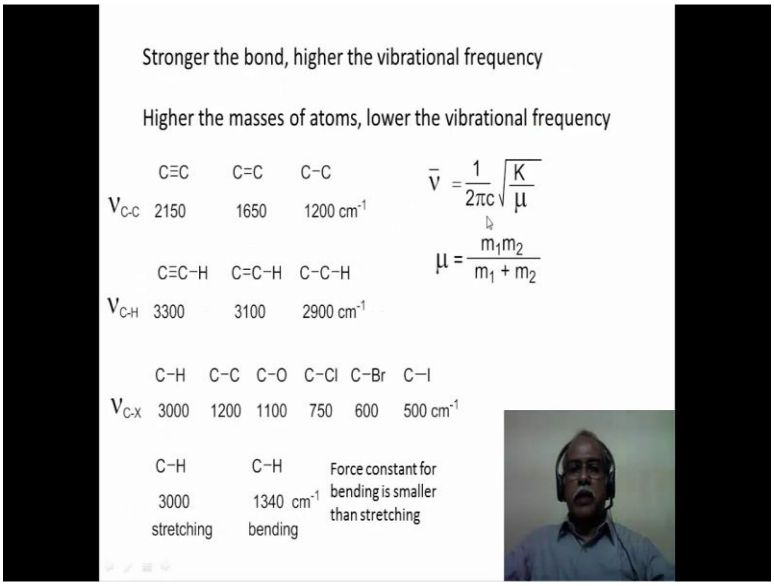

Stronger the bond, higher the vibrational frequency

Higher the masses of atoms, lower the vibrational frequency

	$C\equiv C$	$C=C$	$C-C$
$\nu_{C\text{-}C}$	2150	1650	1200 cm^{-1}

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

	$C\equiv C-H$	$C=C-H$	$C-C-H$
$\nu_{C\text{-}H}$	3300	3100	2900 cm^{-1}

	$C-H$	$C-C$	$C-O$	$C-Cl$	$C-Br$	$C-I$
$\nu_{C\text{-}X}$	3000	1200	1100	750	600	500 cm^{-1}

$C-H$	$C-H$
3000 stretching	1340 cm^{-1} bending

Force constant for bending is smaller than stretching

So, from this equation one can come to the conclusion that stronger the bond, higher will be the vibrational frequency of that particular bond. Higher the masses connected to a particular bond, the atoms that are connected to a particular bond, lower will be the vibrational frequency because of the frequency is dependence, directly proportional to the force constant and inverse relation to the reduced mass of the two atoms that are connected to each other. Now if we use this argument, then one can easily predict the C triple bond C, C double C and C single bond C, what will be the order of the frequencies of the C C stretching of this class of compounds.

Now, C triple bond C is the much stronger bond compared to a C double bond C, which is stronger than the C single bond C. In other words, the force constant is much higher for a triple bonded system compared to a double bonded system, which is stronger than a single bonded system. If this is the order of bond strength, in other words, going from right to left, if the K value keeps increasing, then the stretching frequency should also correspondingly increasing. In fact, that is what one sees. The C triple bond C appears at twenty one fifty inverse centimeter. The C double bond C appears in the region of one thousand six hundred and fifty. Whereas, the C single bond C appears in the region of one thousand two hundred inverse centimeter.

Now, if we consider the CH bond strength of acetylenic bond compared to olefinic CH bond and alkanic CH bond, once again the CH bond of the acetylenic system is much stronger than the CH bond of the olefinic system, compared to the CH bond of a paraffinic system. So, that is also reflected in the; that is also reflected in the stretching frequency being higher for the acetylenic CH, compared to a olefinic CH which is 3100 and compared to a alkanic CH which is 2400, 2900 inverse centimeter. Now, these two parameters essentially vary the K value. In other words, as you go from right to left the force constant keeps increasing whereas, the next two examples are essentially related to the mass; that are reduced to mass, for example.

As you go from CH to CI, the identity and the mass of the atom that is attached to carbon keeps increasing hydrogen, carbon, oxygen, chlorine, bromine and iodine. In other words, keeping carbon as constant we are essentially varying the mass that is attached to the carbon. Therefore, the reduced mass keeps increasing as you go from left to right. As the mass increases, the frequency should be lower for given comparable systems of this kind, for example.

So, as the mass increases from hydrogen to iodine, iodine is the heaviest atom element in this particular series. So, you can see the lowest frequency for the C iodine bond compared to a CH bond. In other words, the stretching frequency of CH bond is about three thousand, CO bond is eleven hundred, CBr point is 600 and finally CI bond, which is the heaviest element among halogens, for example, comes around 500 inverse centimeter or so.

Now, the force constant for the bending is generally much smaller than the stretching kind of a vibrational variation. So, for, if the force constant for bending is smaller than the stretching, then the bending vibration should come at a lower frequency compared to the stretching vibrations. In fact, the CH stretching vibration comes around 300 inverse centimeter, whereas the CH bending vibration comes around 1340 inverse centimeter.

So invariably for all the functional group, the bending modes of vibration is always at a lower frequency, compared to the stretching. For example, the carbonyl stretching and carbonyl bending also will have similar kind of a difference in terms of the carbonyl stretching coming at a higher frequency compared to a carbonyl bending mode which is coming at a lower frequency. So, these two parameters namely the force constant and the reduced mass can be effectively used to predict the order of frequency changes in a given series of comparable system like this; what is illustrated in this particular slide.

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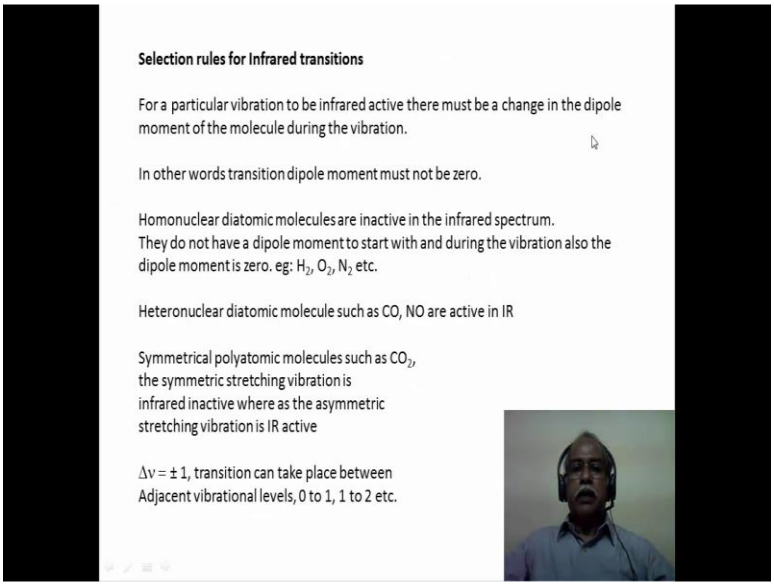

Selection rules for Infrared transitions

For a particular vibration to be infrared active there must be a change in the dipole moment of the molecule during the vibration.

In other words transition dipole moment must not be zero.

Homonuclear diatomic molecules are inactive in the infrared spectrum.
They do not have a dipole moment to start with and during the vibration also the dipole moment is zero. eg: H_2, O_2, N_2 etc.

Heteronuclear diatomic molecule such as CO, NO are active in IR

Symmetrical polyatomic molecules such as CO_2,
the symmetric stretching vibration is
infrared inactive where as the asymmetric
stretching vibration is IR active

$\Delta v = \pm 1$, transition can take place between
Adjacent vibrational levels, 0 to 1, 1 to 2 etc.

Now, let us look at the selection rules for the infrared transition. For a particular vibration to be infrared active, there must be a change in the dipole moment of the molecule during the course of the vibration. So, symmetrical vibrations can be easily ruled out because they will have zero dipole moment change because of the symmetrical nature of the molecule as well as the symmetrical nature of the stretching. For example, a symmetrical stretching of carbon dioxide, where the carbon dioxide, to start with does not have any dipole moment and symmetrical stretching is not going to change any dipole moment. So, essentially the transition dipole moment will be zero. So, the symmetrical stretching frequency of carbon dioxide will essentially infrared inactive in terms of the vibrate, the selection rules not allowing it to happen in the symmetrical stretching of carbon dioxide vibration.

Now, why should that the transition dipole moment be non-zero? In fact, when the electromagnetic radiation is interacting with the vibrational level, it is the electric vector component of the electromagnetic radiation that is going to interact, so unless there is a change in the dipole moment or if unless there is a transition dipole moment, the electrical vector cannot interact properly with the molecules in terms of zero dipole moment of the molecules. So, as a result of that absorption will not take place.

So, the essential condition for an infrared, vibration to be infrared active is that it should have a change in the dipole moment during the course of the vibration. That is why it is homonuclear diatomic molecules are inactive in the infrared spectrum because they do not have a dipole moment to start with. And, during the course of the vibration also there will not be any dipole moment or change of dipole moment will be zero. So H two, O two, nitrogen and so on, these kind of a homonuclear diatomic molecule are inactive as well as the infrared spectroscopy is concerned.

Now, heteronuclear diatomic molecule, something like carbon monoxide, nitrous oxide and so on, they are active in the infrared because they have a permanent dipole as well as a change in the dipole moment, when the stretching between the carbon oxygen bond or the nitrogen and oxygen bond occurs during the course of the stretching. Symmetrical poly atomic molecule such as carbon dioxide, the symmetric stretching is infrared inactive, where as the asymmetric stretching is actually vibrationally active or IR active.

The transitions can occur between adjacent vibrational level. In other words, it can go from 0 to 1, 1 to 2 and so on. And, going from 0 to 2 and 0 to 3 is normally not allowed in the case of infrared spectroscopy.

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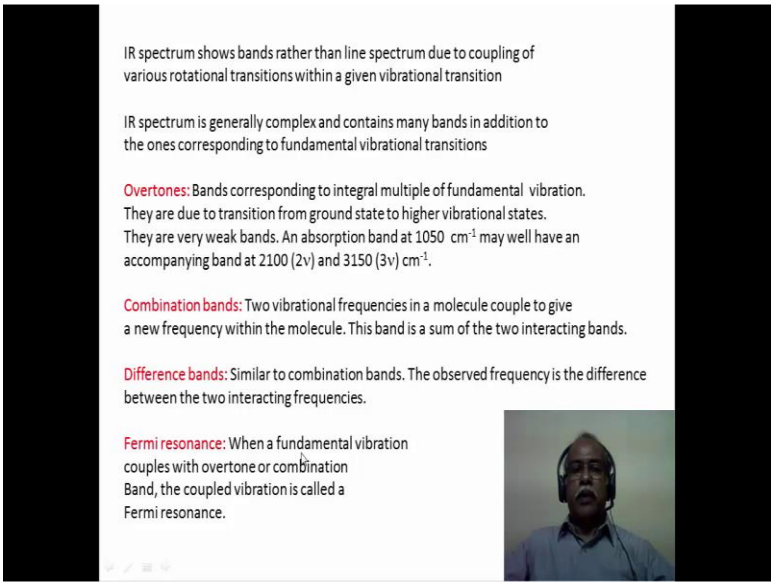

IR spectrum shows bands rather than line spectrum due to coupling of various rotational transitions within a given vibrational transition

IR spectrum is generally complex and contains many bands in addition to the ones corresponding to fundamental vibrational transitions

Overtones: Bands corresponding to integral multiple of fundamental vibration. They are due to transition from ground state to higher vibrational states. They are very weak bands. An absorption band at 1050 cm^{-1} may well have an accompanying band at 2100 (2ν) and 3150 (3ν) cm^{-1}.

Combination bands: Two vibrational frequencies in a molecule couple to give a new frequency within the molecule. This band is a sum of the two interacting bands.

Difference bands: Similar to combination bands. The observed frequency is the difference between the two interacting frequencies.

Fermi resonance: When a fundamental vibration couples with overtone or combination Band, the coupled vibration is called a Fermi resonance.

So, infrared spectrum should have only fine lines or fewer numbers of bands or fewer numbers of lines should be seen. But, this is not the case. Infrared spectrum can be very complex in nature. The infrared spectrum actually shows the band structure, rather than line structure due to coupling of rotational transitions within the given vibrational level. In other words, although rotational transitions occur totally in a different energy region, they cannot be completely decoupled from the vibrational transitions because within the same molecule, the transition and the vibrational transitions can be coupled together. So, as a result of that the infrared spectra do not appear as a line spectrum, rather gives bands of infrared transitions in the vibrational; vibration level transitions in the infrared spectrum.

Infrared spectrum is generally very complex and contains many bonds, in addition to the one corresponding to the fundamental vibrations transitions. For example, you can have a combination of overtone bands, combination bands, difference bands and fermi resonance band. These are various types of band that can appear in the infrared spectrum.

Let us consider one by one. Suppose, let us assume there is a stretching absorption band at 1015 inverse centimeter. This may very well have the accompanying bands, which are much weaker bands which are called the second harmonic and the third harmonic, occurring at twice the frequency at the primary fundamental vibration. 1050 is the fundamental vibration. So, one can expect 2100 to be the second harmonic, 3150 to the third harmonic. So, these bands can also appear along with 1050 band.

The 1050 band, of course will be the most intense band. As the second harmonic and third harmonic progresses, the intensity falls down. And, also the broad, the band width also keeps increasing as you go from the fundamental vibrations to the first harmonic and second harmonic to the third harmonic. The band width also keeps increasing. This is essentially due to the transition from the ground state to the higher vibrational state, which is generally forbidden. But, there are mechanism by which this can happen. And, that is why you see the second harmonic and the third harmonic vibration.

Suppose, if two vibrational frequencies are there in the molecule, they can couple to give a new frequency under certain conditions. Not all the time two frequencies couple to give a third frequency, but there are conditions under which two vibrational frequency of a molecule can give a new frequency within the molecule. This band is called the sum of the two interacting molecule, or the combination band is obtained. The difference band is exactly the opposite. The two bands, which two vibrational frequency, the difference can be observed. The observed frequency is the difference between the two interacting frequencies. In other words, this is similar to a combination band, except this is addition and this is subtraction in terms of the two frequencies which are interacting or coupling to give a third frequency.

Fermi resonance is essentially when a fundamental vibration couples with the over tone or a combination band. The coupled vibration is what is known as the fermi resonance. Fermi resonance is fairly common in carbonyl compounds. We will see some examples of fermi resonance happening, when we are dealing with the carbonyl frequencies of various organic compounds.

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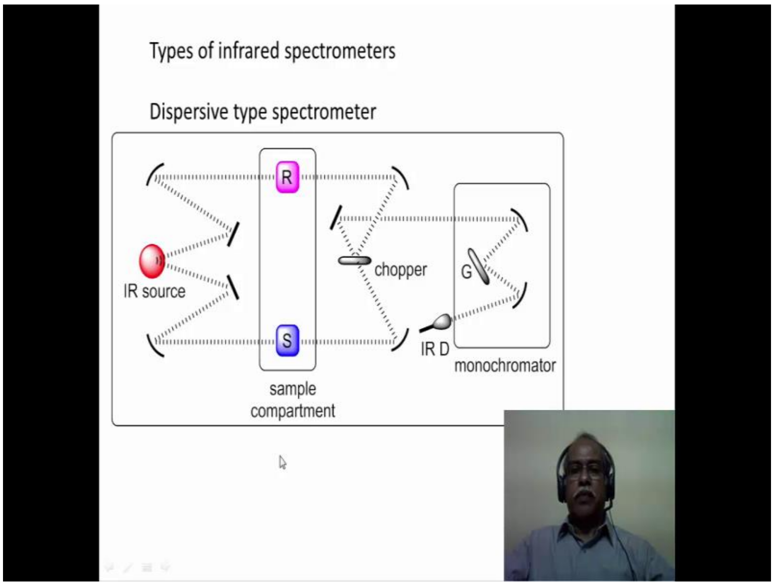

Types of infrared spectrometers

Dispersive type spectrometer

Now, let us come to some understanding of the basic layout of an infrared spectrometer. There are two types of spectrometers available. Just like we have two types of NMR spectrometer, where you have a continuous wave NMR spectrometer and the FT-NMR spectrometer, this is a continuous wave equivalent of the infrared spectrometer. This is called the dispersive type spectrometer. Essentially, what you have is a infrared source which is a globar or a heated coil, which essentially produces thermal energy which is the infrared energy. And, these are mirrors which are kept to reflect the infrared radiation. So, you have two beams which can be reflected, one to the sample, the other one to the reference. Suppose, if the sample is dissolved in a chloroform as a solvent, the reference will be chloroform or if the sample is made in the form of a nujol mull, the reference can be simply a nujol mull. We will see all the sample preparation in a minute.

But, let us assume that there are two beams which are coming from the infrared source, one passing through the reference sample, reference compartment, the other one passing through the sample compartment. The sample is kept here and the blank solvent is kept here, for example. And, both these beams after passing through the sample, it goes through the mirror and goes through a chopper. The chopper, essentially alternates the beam that is falling on to the grating.

For example, when the chopper is open, this beam will go in and that will hit the grating. Or, if the chopper is close to this beam will essentially go and head hit the, get reflected on to the grating. Grating is the dispersive mode grating. So, essentially it changed. It resolves the frequencies of the infrared region. And, the frequencies one after the other by tuning the grating, for example, falls on the infrared detector. The detector detects and puts it in the form of a signal, which is recorded as in infrared spectrum.

So, this is the sample compartment essentially and this is a monochromator compartment of the infrared spectrometer and this is the double beam spectrometer. If you observe carefully, there are two beams coming, one through the sample, sorry, one through the reference and the other one through the sample. The both the beams, essentially enter the grating as well as detector alternatively because of this chopper. So, one can have i 0 as well as i recorded simultaneously, by which ever beam is falling on the grating and the infrared detector. If it is coming from the reference beam that will be the i 0 and if it is coming from the sample beam that will be the i. So, one can easily determine the logarithm of i 0 by i to look at the absorbance values of the various frequencies which are generated by the grating, in terms of dispersion of the infrared radiation by the grating.

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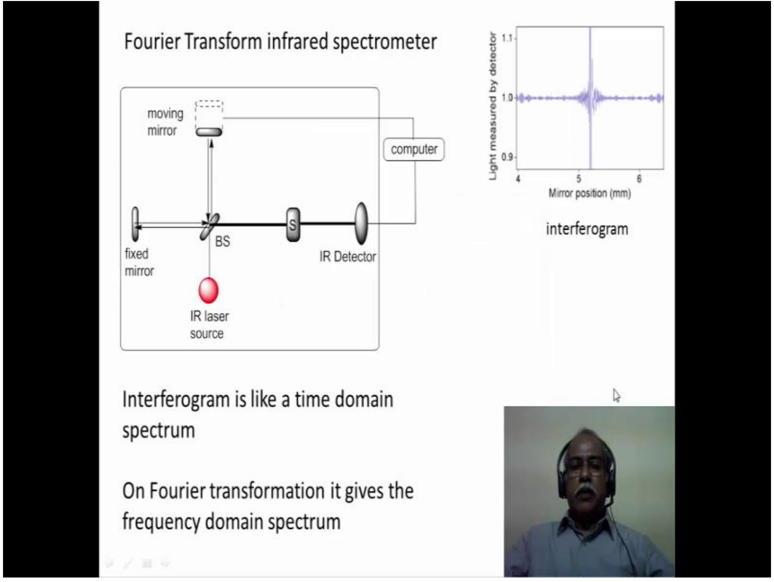

Fourier Transform infrared spectrometer

Interferogram is like a time domain spectrum

On Fourier transformation it gives the frequency domain spectrum

In the other spectrometer, other type of spectrometer which is called the Fourier transform infrared spectrometer. This is the most modern spectrometer that is available. In fact, this is an outdated spectrometer. Normally in commercial spectrometers, this is no longer available. Only the infrared spectrometer, which is Fourier transform infrared spectrometer is readily available these days.

Here, there is a source of laser which falls on the beam splitter. Essentially, the beam splitter splits the laser beam into 50 percent. Each of these two beams that are indicated, one beam passes through a mirror and gets reflected back to the beam splitter. The other one passes through a mirror and gets reflected. But, this mirror is not in a fixed position. This is a movable mirror, whereas this is a fixed mirror.

So, when these two beams are mixed on the beam splitter, it produces interferogram pattern. And, interferogram pattern is essentially looking like this one. So, the interferogram pattern is essentially sent to the detector and recorded as a blank. And then, it is sent through a sample and recorded, which is the actual sample signals that you get. So, the interferogram is something like a time domain spectrum of the infrared spectroscopy. When it is fourier transform, it gives the frequency domain spectrum by conversion of the interferogram into the frequency domains of the various frequencies, which are observed by the sample is essentially detected in the infrared spectrometer.

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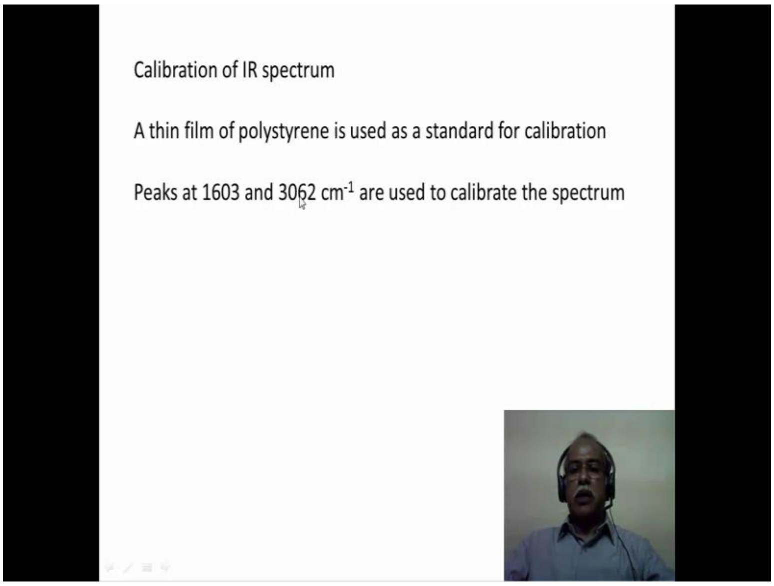

Calibration of IR spectrum

A thin film of polystyrene is used as a standard for calibration

Peaks at 1603 and 3062 cm^{-1} are used to calibrate the spectrum

In order to calibrate the infrared spectrum, a thin film of polystyrene is generally used. This is a standard sample and the calibration peaks at 1602, which is because of the C double bond C stretching frequency of the polystyrene. The CH stretching frequency of the polystyrene, which appears at 3062, these two peaks are used essentially to calibrate the infrared spectrum.

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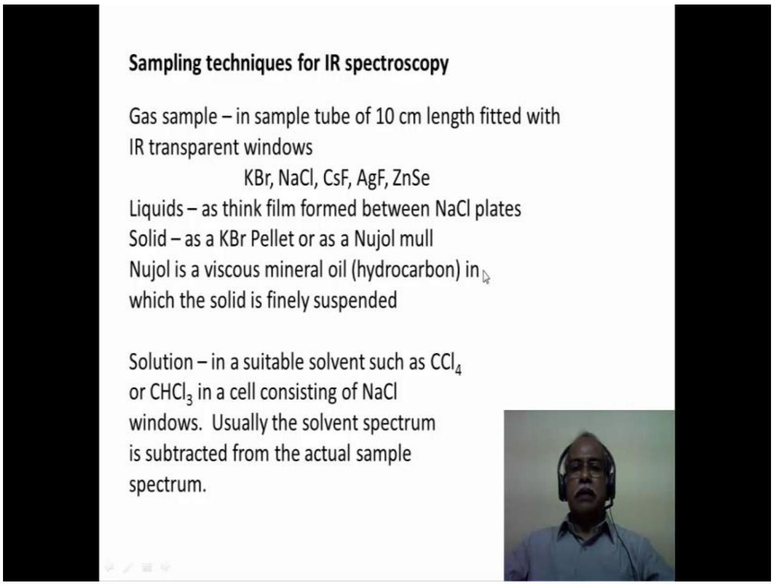

Sampling techniques for IR spectroscopy

Gas sample – in sample tube of 10 cm length fitted with IR transparent windows

KBr, NaCl, CsF, AgF, ZnSe

Liquids – as think film formed between NaCl plates

Solid – as a KBr Pellet or as a Nujol mull

Nujol is a viscous mineral oil (hydrocarbon) in which the solid is finely suspended

Solution – in a suitable solvent such as CCl_4 or $CHCl_3$ in a cell consisting of NaCl windows. Usually the solvent spectrum is subtracted from the actual sample spectrum.

Sampling technique is extremely important in infrared spectroscopy because many glass vessels or quartz vessel do observe the infrared radiations. So, one cannot use glass vessels or quartz vessels for the infrared radiation. One has to use vessels which are made up of materials which do not observe or predominantly do not absorb the infrared radiation.

So, essentially this kind of inorganic salts or inorganic materials are used as transparent windows or transparents; materials made out of the inorganic substances which are potassium bromide, sodium chloride, cesium chloride, silver fluoride, zinc selenide and so on. They are essentially used as they are made use of as material for making the cells and windows of the infrared sampling techniques.

Now, samples such as gas samples, liquid samples as well as solid samples can be measured using an infrared spectrum. If it is a gas sample, it is simply a 10 centimeter tube fitted with the IR transparent windows, which are made out of this material is what is used. The reason, why 10 centimeter cell is necessary because as a gas sample, typically the concentration is fairly low, the atmospheric pressure, one measures the gas sample, the concentration is going to be so. One needs to have a longer path length. That is why a 10 centimeter path length is generally used.

Liquids can be measured as it is as a thin film. When a (Refer Time: 29:20) of the thin film between sodium chloride plate is made, that sodium chloride plate essentially acts as a transparent window for the infrared radiation. Or, the solid can be made into the form of a pellet by mixing the sample with the potassium bromide. Less than one percent of the sample is mixed with the potassium bromide and it is crushed into a fine powder and made in the form of a pellet in a compressing machine. And, that can be used as it is in the infrared spectrometer. Or, the solid can be dispersed in a hydrocarbon medium which is known as nujol. Nujol is a very viscous mineral oil, which is consisting of saturated hydrocarbon. A fine suspension of the solid on the hydrocarbon mineral oil is what is known as nujol mull. And, that can be used for measuring the solid state materials.

One can also make the infrared spectrum using solutions. When the substance is dissolved in carbon tetra chloride and chloroform, the cell consisting of sodium chloride windows can be used to measure the solution; solution phase spectrum can be measured using this particular technique. Usually, solvent spectrum is subtracted from the actual sample spectrum because the solvents also have some windows in which they absorb the infrared radiation. So, that has to be compensated by subtracting the solvent spectrum from the actual spectrum of the infrared spectrum.

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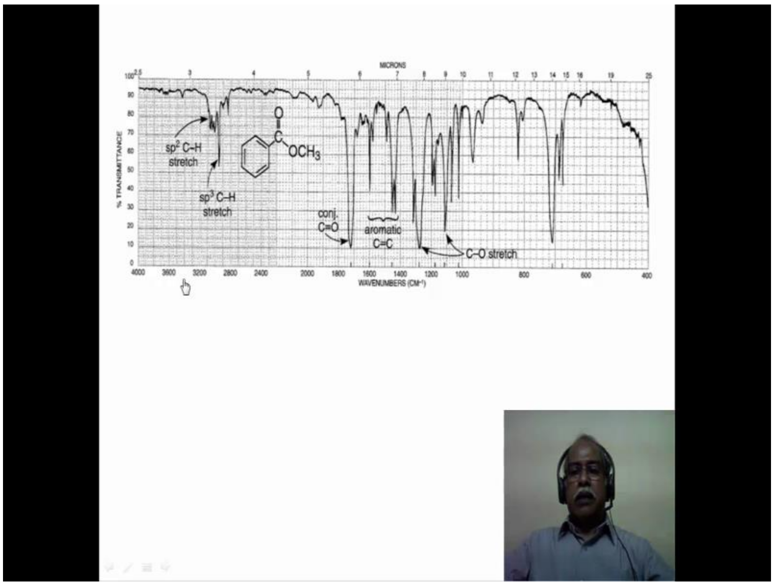

This is a very characteristic infrared spectrum, for example. This is, essentially the wave number is plotted which is a energy scale against percentage transmittance. This is a convention that is normally used in the infrared spectral plotting. One plotted plots the wave number and not the wavelength or the frequency. And, one always plots the percentage transmittance, rather than absorbance. One can plot it in absorbance if you want to measure quantitative terms, the infrared spectroscopy. So, depending upon the usage it is normally the transmittance. But, one can also measure it in absorbance mode also the infrared spectrum.

They essentially have different kinds of bands in the infrared spectrum. And, these bands are responsible for the various stretching frequencies of the molecule, the various stretching modes of the different kinds of bonds which are mentioned. For example, you have a sp 2 CH stretch, sp 3 CH stretch, a carbonyl stretching band and aromatic CC stretching band and CO stretching band. So, the different kinds of stretchings that occur in the molecule and the infrared absorption takes place at a select frequency, which puts out the signal in the infrared spectrometer to give this kind of a spectrum.

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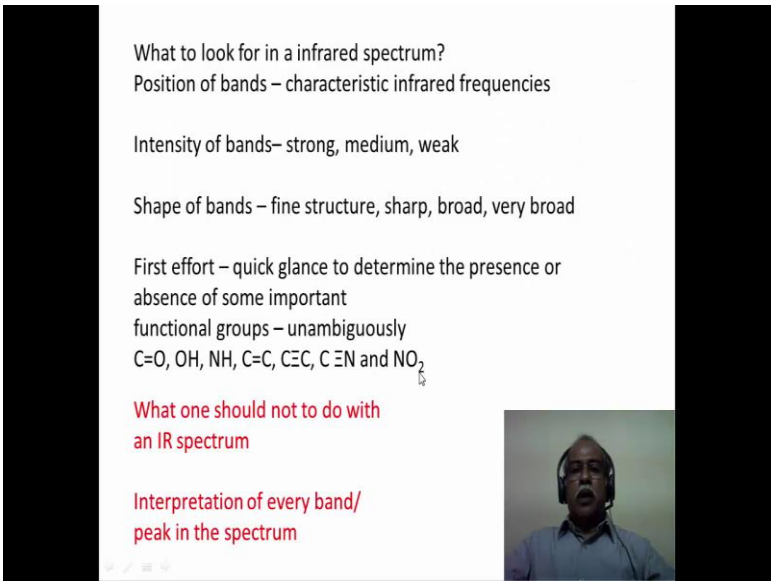

What to look for in a infrared spectrum?
Position of bands – characteristic infrared frequencies

Intensity of bands– strong, medium, weak

Shape of bands – fine structure, sharp, broad, very broad

First effort – quick glance to determine the presence or
absence of some important
functional groups – unambiguously
C=O, OH, NH, C=C, C≡C, C≡N and NO_2

What one should not to do with
an IR spectrum

Interpretation of every band/
peak in the spectrum

Now, what are we looking for in an infrared spectrum? Infrared spectrum is fairly complex. To interpret this spectrum, every one of the peak in the spectrum to be interpreted is humanly impossible task or a very time consuming task. So, what one looks for is first the intensity of the bands; are they strong bands, medium bands or weak bands? For example, this would be a strong band, this would be a medium band and this would be a very weak band which is a shoulder band, for example. So, the type of band that we are looking at in terms of the intensity or the strength of the band is important.

The shape of the band is important. Whether it has a fine structure, whether it is a broad or very sharp or very broad, this is needs to be very clearly defined. In this cases, most of the; this is a fairly broad band, whereas this is a sharp band. And, one has to look for the kind of patterns that one can expect for certain kind of transitions in the infrared region by looking at the shape of the bands. We will see some of these aspects, a little more detail when we actually go into the functional group problems.

In the very first effect, effort, a very quick glance to determine the presence or absence of some of the important functional group and ambiguously can be done. For example, carbonyl functional group, whether it is there or not, it will typically appear in this particular region between 1600 to 1800 inverse centimeter region, wave number region is where it will appear. Similarly, OH has a special region, NH has a special region, C double bond C has a special region. Likewise, these functional groups can be unambiguously detected. And, one can tell from the infrared spectrum, whether this functional groups are present or not in a definitive manner, for example. So, that is what the infrared spectrum is generally used for.

What is that one should not do with an infrared spectrum? One should not interpret every single peak in infrared spectrum. For example, if we start interpreting every one of these peaks that is appearing in the infrared spectrum, that would be extremely difficult to do. And, that is something one should not attempt. One should look for the prominent bands, which are due to certain functional groups in the organic molecule.

So, what we have seen in this particular module is the introduction to infrared spectroscopy and the basic principle behind infrared spectroscopy. What is it used for in terms of structure elucidation problem? How does a spectrometer look like in terms of the layout, the two types of spectrometers? And what are the sampling techniques? These are the few things that we have seen in the module. In the next module, we will start with the functional group analysis of various types of functional groups.

Thank you very much for your attention.