Infrared Spectroscopy for Pollution Monitoring
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Lecture-14
Infrared spectroscopy–Introduction

Hello everyone, in continue our discussion on infrared I was teaching you that if there are n number of atoms in an organic compound. We have about 3n-6 vibrational energy levels and a simple compound like methane would have 9 vibrational modes and benzene would have about 30 possible vibrational bands. So, the vibrations these vibrations must cost a change in the dipole moment if I have to see an infrared spectrum.

So, molecules containing symmetrical groups may not be infrared active, so compounds like ethylene very symmetrical compound carbon dioxide is a very symmetrical compound. So, you will not see any infrared spectrum for carbon dioxide.

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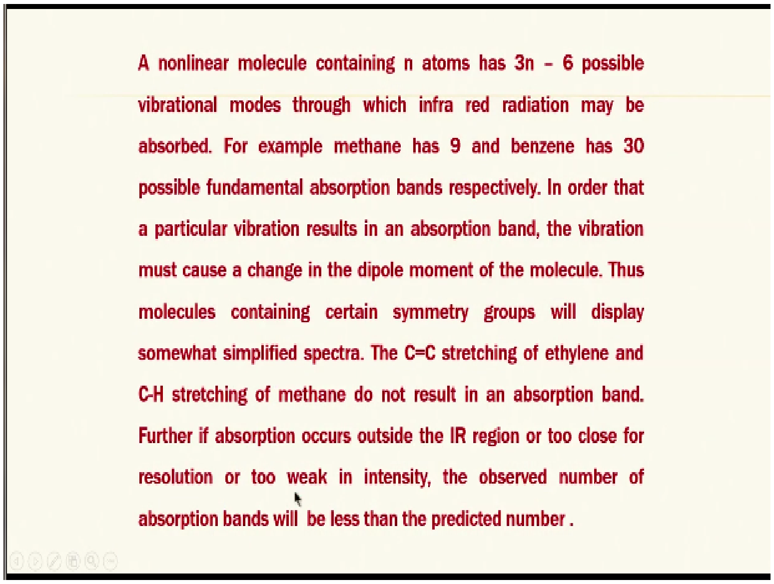

A nonlinear molecule containing n atoms has 3n – 6 possible vibrational modes through which infra red radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. Thus molecules containing certain symmetry groups will display somewhat simplified spectra. The C=C stretching of ethylene and C-H stretching of methane do not result in an absorption band. Further if absorption occurs outside the IR region or too close for resolution or too weak in intensity, the observed number of absorption bands will be less than the predicted number.

Similarly for if there are absorption occurs outside the sometimes outside the IR region sometimes these things do not show peak sometimes they occur they are too weak to show up in the infrared spectrum. Such peaks also will not be observed, so the observed number of absorption peaks are much less than the predicted number. So, but still they are quite large.

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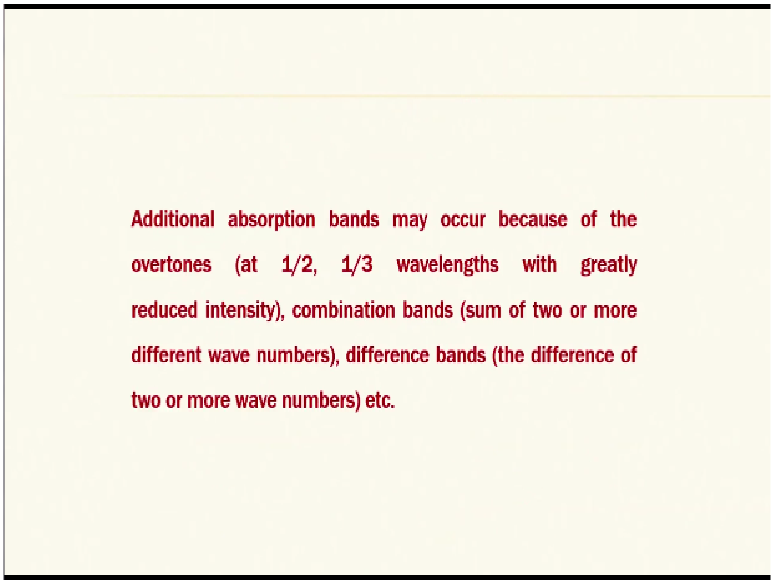

Additional absorption bands may occur because of the overtones (at 1/2, 1/3 wavelengths with greatly reduced intensity), combination bands (sum of two or more different wave numbers), difference bands (the difference of two or more wave numbers) etc.

Further you will see that additional absorption bands may occur because of the overtones that is I had told you that the overtones are peaks at 1 and half to 1/3 wavelengths with greatly reduced intensity of the same IR peaks sometimes I get combination bands that is sum of 2 are more different wave numbers is another peak. Sometimes I get difference bands difference of 2 or more wave numbers etc.

So, these are additional peaks and 1 requires a special eye or special knowledge to interpret these peaks. It is not everybody they can recognize each and every peak in infrared spectrometry. So, we are going to talk about molecular vibrations in infrared spectroscopy. So, how we essentially visualize an infrared spectroscopy or vibrations, a molecule essentially resembles a set of balls of varying masses.

So, this is a very standard way of representation of the compounds or atoms, you must have seen in number of books that a hydrogen is represented as 1 ball and oxygen is represented as another ball etc.

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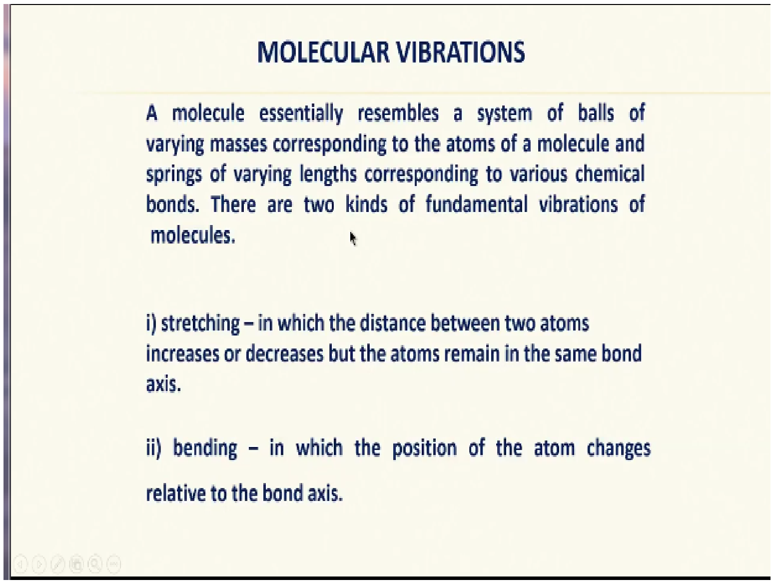

MOLECULAR VIBRATIONS

A molecule essentially resembles a system of balls of varying masses corresponding to the atoms of a molecule and springs of varying lengths corresponding to various chemical bonds. There are two kinds of fundamental vibrations of molecules.

i) stretching – in which the distance between two atoms increases or decreases but the atoms remain in the same bond axis.

ii) bending – in which the position of the atom changes relative to the bond axis.

So you look at the structures of the molecules, we normally represent them as balls of different sizes because hydrogen has got only one atomic weight and oxygen has got 16. So, the ball of oxygen should be weighing should be bigger than hydrogen something like that, so essentially what we are talking is a functional group or an organic model of an organic compound must be composed of several balls of varying sizes.

And connected with springs, that is the model you can buy them in the market they are available and that is I am going to explain to you now. So a molecule is nothing but number of balls representing a functional group. So for methane what I have is I have 1 carbon atom at the center and then I make 4 holes and then 3 hydrogen at the bottom like a pyramid 1 at the top that is tetra hydra molecule.

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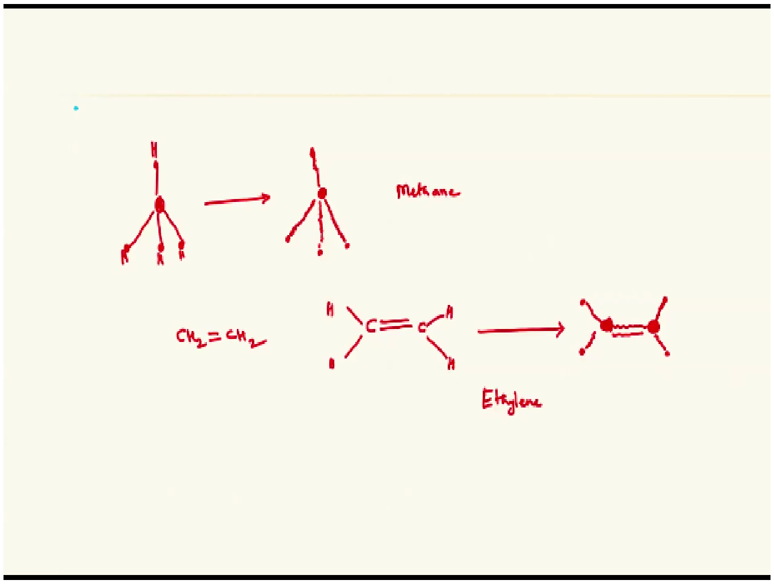

So, I can show you some of those pictures, so I can write a compound like methane 1 ball okay, then 1 bond here, 1 bond here, 1 bond here. This is hydrogen, this is 3rd hydrogen okay and there is 1 more hydrogen at the top. So, this is how we represent, so each hydrogen is represented as a ball and these are connected through a line and instead of line I can represent the whole thing like this, this is my carbon, this is 1 spring connected to hydrogen atom.

And another spring connected to another hydrogen atom connected to another hydrogen atom. So, this is how this is known as ball model, similarly I can write for this is for methane. Now suppose I want to write to benzene or ethylene, so what is the formula for ethylene CH2 double bond CH2 I have 1 carbon here and then 1 carbon here, 1 double bond and 1 hydrogen here, 1 hydrogen here okay.

And this is hydrogen, this is another hydrogen, so this I can represent as ball model the 1 big carbon okay and 1 more big carbon atom and then the hydrogen atom, second hydrogen, this is 3rd hydrogen, this is 4th hydrogen. So I can represent another model another bond like this, this is ethylene like that I can make a ball model for many of these things I can represent them like this.

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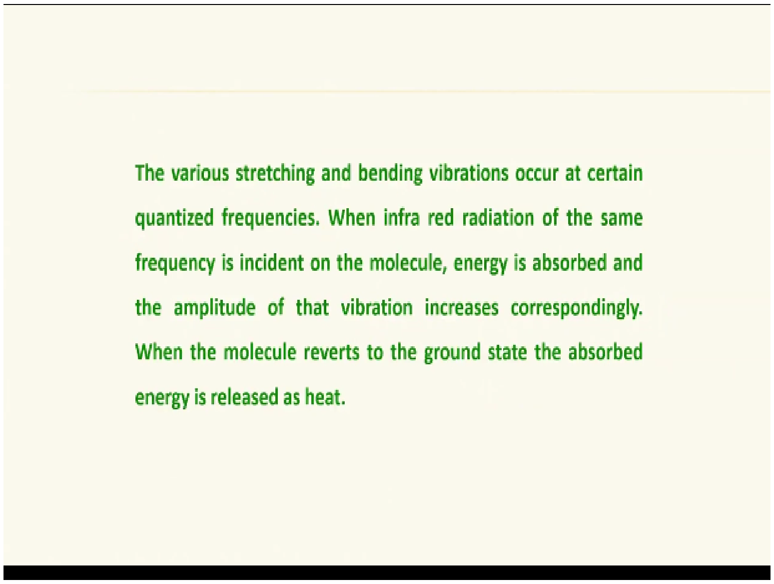

The various stretching and bending vibrations occur at certain quantized frequencies. When infra red radiation of the same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration increases correspondingly. When the molecule reverts to the ground state the absorbed energy is released as heat.

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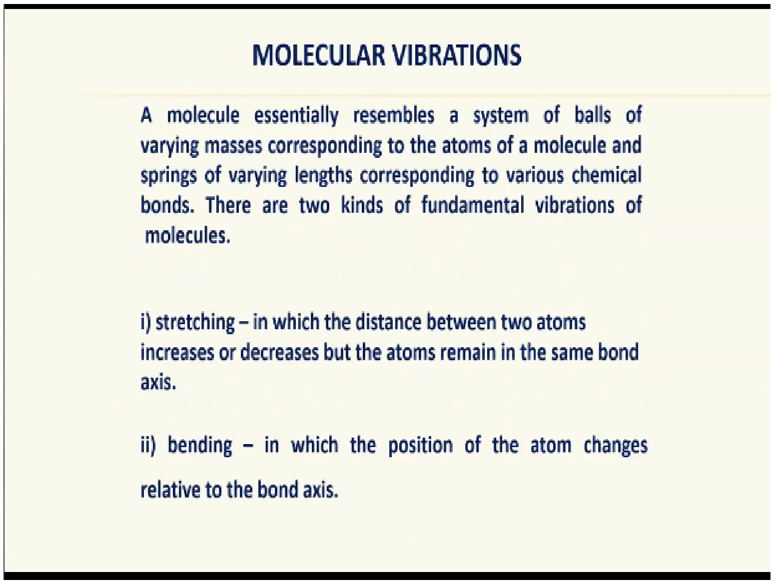

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So, the molecule essentially resembles a system of balls of varying masses corresponding to the atoms of a molecule and springs of varying lights corresponding to various chemical bonds. So, there are 2 kinds of fundamental vibrations 1 is known as stretching. So another number is known as bending now you can imagine I am holding 2 balls here 1 like this, this is 1 ball and I have 1 more ball here like this.

These 2 are connected by a bond I can pull them I can pull them away pull them nearer. So, like that this is known as stretching, very simple conception a stretching and another 1 is bending like this or they can bend towards you or they can bend towards me also. So there are different kinds of stretching and bending operations occur 1 can stretch like this another can bend like this different ways of bending.

So, this you can imagine only if you imagine that they are balls attached with a spring then only you can do stretching and bending vibrations. That is like simplified model it is not the actual model, so the various kinds of stretching and bending vibrations occur at different quantized frequencies. So when infrared radiation of the same frequency is incident on the molecule, so you can imagine.

That the bonds are like this they are all always stretching now I have infrared radiation falling on this system. So, the stretching vibration when it is matching the frequency of the infrared is matching with the stretching frequency then excitation can occur, excitation to next higher energy level. So at that time infrared radiation is absorbed and the amplitude of the vibration increases correspondingly depending upon the amount of electromagnetic radiation.

That is IR absorbed, so when the molecule reverts to the ground state the absorbed energy is lost this I have explain to you earlier. That the energy is sometime lost to other molecules or as heat or in some other fashion usually by collision with other molecules present in the same sample or matrix components okay quite often the molecule reverts to the ground state where the absorbed energy is released as heat, heat also is quite possible.

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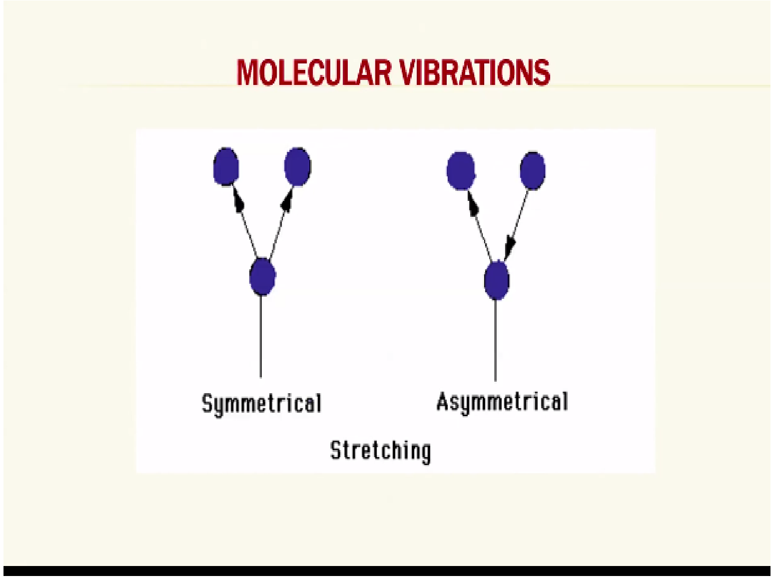

MOLECULAR VIBRATIONS

So, what are different kinds of vibrations that can occur in a given system, look at this slide now. So, here I am representing a model I am also showing you the stretching types, so here I am showing you the stretching vibration. Here is my central ball you can imagine this is CHO okay, you can imagine or CH2 here it can be a carbon atom and this can be a hydrogen atom and this can be another hydrogen atom.

So, the 2 hydrogen atoms are connected to the carbon atom and this is the axis that is the compound axis organic compound axis how you imagine the compound this is only a functional that means it is only a part of the organic compound okay. So now I have look at these 2 figures carefully you can see that the bond between this 1 and this 1 is stretching towards top and this is also stretching towards the top.

That means both of them are getting pulled simultaneously like this. So the stretching takes place in the same direction simultaneously but look at the other picture now. Here what is happening the central ball is here and hydrogen is here another hydrogen is here when this is stretching this is contracting. So, imagine when this is stretching this is contracting like this. So, a dynamic picture of a stretching frequency can be both of them going simultaneously going up and up.

And down or this goes up this comes down like this known as symmetric stretching okay. So, there are 2 kinds of infrared peaks we will get if the stretching is symmetrical I get a 1 peak and if the stretching is asymmetrical I get another peak. Obviously the energy required for this kind of transition is different isn't it, so I will get 2 peaks. So, good organic chemist can recognize a stretching frequency among the stretching frequency 1 can recognize a symmetrical stretching and another is asymmetrical stretching.

Asymmetrical stretching will occur at a it requires less energy whereas asymmetric stretching will require more energy. So less the peak at less energy would be appearing at longer wavelength and the peak at more energy the peak corresponding to more energy transition would appear at the shorter wavelength. So these are the molecular vibrations involving stretching okay.

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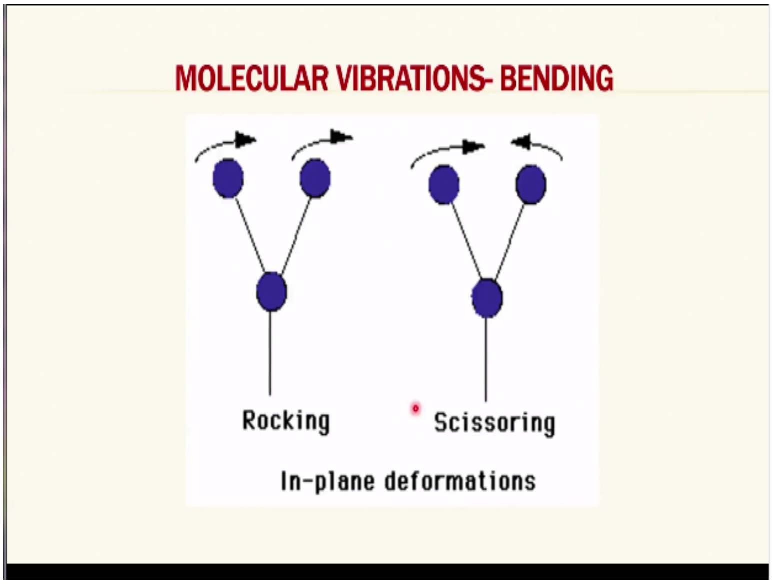

MOLECULAR VIBRATIONS- BENDING

In-plane deformations

Now look at the molecular vibrations of another kind I had explain to you earlier at the vibrations can occur in stretching and bending. Now I am going to show you the bending vibrations, so how do these bending vibrations appear, you look at the slide now. Here I am showing 2 types of vibration okay, here as usual my central atom is here axis is here 2 hydrogen bonds or 2 balls are here.

Now imagine I have a carbon atom here like this okay, now both of them are going like this, both of them are coming like this okay. This is known as rocking, they are in plane, in the same plane is not it, the excess is at the bottom and they are like this. In the same plane I am pushing them this side and then I am taking them back this side, this is known as rocking. So, the even in rocking I have different another possibility.

That when 1 is coming this side other may also be moving away from it relatively or coming towards it relatively. Now I can show you that very simply like this, this is known as scissoring just imagine like this suppose I increase it more does it not look like a scissor my hands okay. Now the other one is rocking like this, so rocking and scissoring are in plane bending that means they are occur in the same plane.

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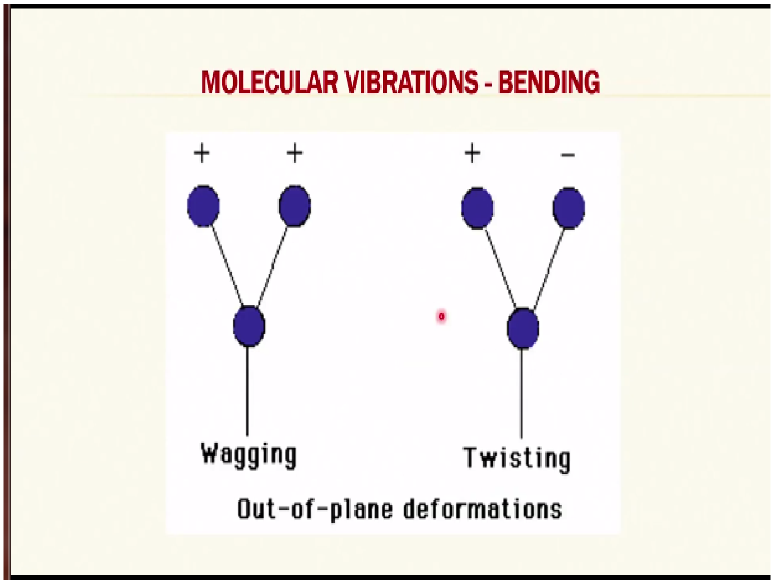
MOLECULAR VIBRATIONS - BENDING

Wagging

Twisting

Out-of-plane deformations

Now I will show you out of plane the deformation this is molecular vibration bending same title I have the 2 types again central ball axis and 2 more hydrogen atoms and similarly another 1. And here you can see that I have put +sign here and 1+ and 1- sign here. Now look at my hands now, earlier I had shown you like this, now I am showing you this is out of plane, imagine your my screen as 1 plane.

I am going behind the screen and coming towards you, so the balls are moving like this, now if I put + sign that means both of them are coming towards you and going back simultaneously okay both of them are going back or coming towards you. Now when I put 1+ and 1- it will be like this, the molecular vibration would be appearing like this. So, this will be this is known as twisting and this is wagging ting, ting, ting like that.

There are different kinds of vibrations that appear these are out of plane deformations, so to just to make sure that you have understood I am going to show them once again to you okay. So, this is symmetrical stretching both of them are stretching away from each other and in this case asymmetrical they are stretching 1 to away, 1 towards these things. And then I have 4 bending vibrations 2 of them are in plane they are known as rocking another 1 is scissoring. And the next 1 is wagging and twisting okay.

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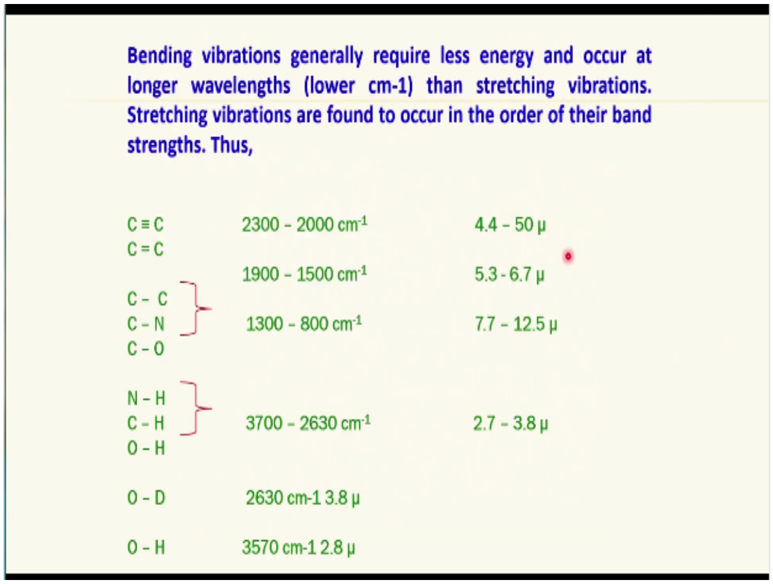

Bending vibrations generally require less energy and occur at longer wavelengths (lower cm-1) than stretching vibrations. Stretching vibrations are found to occur in the order of their band strengths. Thus,

$C \equiv C$	2300 - 2000 cm^{-1}	4.4 - 50 μ
$C = C$		
	1900 - 1500 cm^{-1}	5.3 - 6.7 μ
$C - C$		
$C - N$	1300 - 800 cm^{-1}	7.7 - 12.5 μ
$C - O$		
$N - H$		
$C - H$	3700 - 2630 cm^{-1}	2.7 - 3.8 μ
$O - H$		
$O - D$	2630 cm-1 3.8 μ	
$O - H$	3570 cm-1 2.8 μ	

So, these are the different kinds of vibrations generally occurring in infrared spectroscopy, so what how do I go looking that for which bending which rocking, which is twisting etc. what kind of wavelengths or what kind of transitions can occur. Now how do I recognize all these things means people have studied different compounds and made a table of where such peaks appear.

And then what they find out is bending vibrations is generally require less energies, bending vibration just telling. But stretching frequency must appear at longer wavelength or shorter wavelength. The stretching frequencies must appear at shorter wavelengths that is higher centimeters inverse between 4000, 5000 not 5000, 4000, 3000, 2000 like that. And bending vibrations should occur towards the other end of the spectrum okay.

Now stretching vibrations are also found to occur in the order of their bond strength okay. So, the bond strength are also important, so the bond strengths are also important now you will remember that what I had taught you about single bonds, double bonds etc. Now if you remember the chemistry correctly you know that single bonds or sigma bonds double bonds are Pi bonds.

And then there are acetylene bonds which 2 Pi bonds okay, so then there are atoms or functional groups with non bonded electrons also okay. Now what I have been saying that the stretching and bending vibrations represent the bond strengths. So, suppose I have a single bond, a double bond and a triple bond which 1 would be having maximum bond strength just I am giving you 2 seconds or 3 seconds pause.

We can think of it which one single bond, double bond and triple bond which one would be having higher strength okay. Now I have having 3 seconds are over I want to tell you that single bond is less strong then double bond, double bond is having is more stronger than a double bond is less strong then triple bond. So, among the 3 triple bond is very strong and double bond is less than that and single bond is still less than that.

So, a triple bond would be a bond length in a triple bond would be very small compare to a double bond and that is very small compare to a single bond, single bond would be having larger bond length. So larger bond length means the energy corresponding to that would be less now we will come back to this slide. Now look at the slide here I have carbon-carbon triple bond and carbon-carbon double bond okay.

So in this carbon-carbon triple bond where do I have the infrared peak, the infrared peaks are triple bond is somewhere between 2300 to 2000 centimeters inverse corresponding the micrometers is 4.4 to it should be 5.0 4.4 to 5 microns. I will correct that okay.

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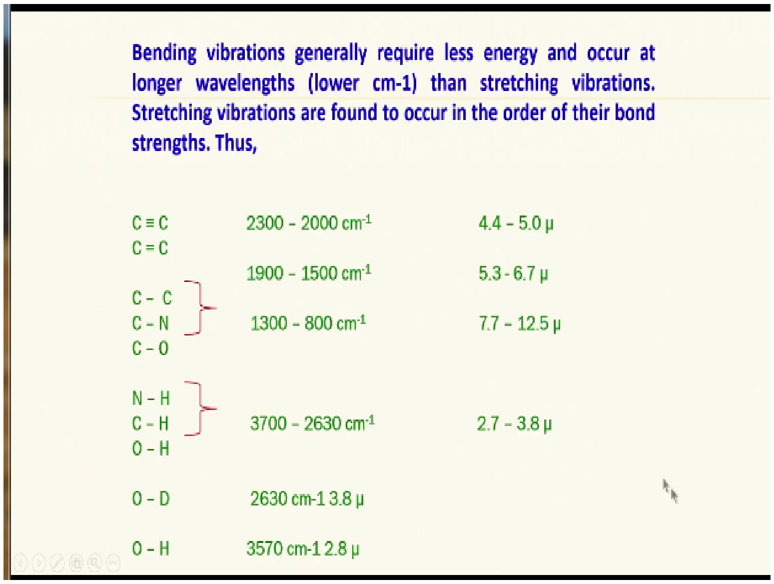

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C ≡ C	2300 - 2000 cm^{-1}	4.4 - 5.0 μ
C = C		
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C - C		
C - N	1300 - 800 cm^{-1}	7.7 - 12.5 μ
C - O		
N - H		
C - H	3700 - 2630 cm^{-1}	2.7 - 3.8 μ
O - H		
O - D	2630 cm-1 3.8 μ	
O - H	3570 cm-1 2.8 μ	

So, it should be 5.0 microns, so carbon-carbon double all double bonds and all triple bonds in a given in organic compounds. If you take their IR spectrum the IR peak should appear between 2000 and 2300 centimeters inverse. This is what we are talking about the appearance of the peaks is double bond or a triple bond should appear at the lower wavelength range. Now look at the next same slide less another concept.

Here I have 3 triple bonds, 3 compounds, 1 is carbon-carbon single bond, 1 is carbon nitrogen single bond and another is carbon oxygen single bond. Now carbon is common here okay and here it is carbon, it is nitrogen, it is oxygen what is the atomic weight of carbon is 12, nitrogen is 14 and oxygen is 16. So when I have this the peaks will appear between 1900 to 1500 centimeters inverse.

And there is 1 more peak appearing somewhere around 1300 to 800 centimeters inverse okay. Now look at this corresponding numbers are microns okay micrometers 5.3 to 6.7 and 7.7 to 12.5. Now compare this double bond position with single bond position, so obviously like our earlier theory of single bond is longer. It is having less energy compare to double bond, so single bond should appear at longer wavelength right.

So, here it is appearing at 1500 compare to 2000 of a double bond, again we go back to this slide. So, this is what it represents okay, so single bond 1900 to 1500 and carbon-carbon you can see this here carbon-carbon single bond, this is carbon-carbon double bond. So, single bond is 1900 carbon-carbon double bond is 2300 to 2000.

Now look at another combination here I have put N-H, C-H and O-H now a hydrogen atom is common in this side okay. And it is a single bond and the atomic weight of nitrogen is again 14, this is 12, this is 16. Now all these single bonds containing hydrogen atom in the functional group appear between 3700 to 2630 centimeters inverse okay. So, the range is important in this case but not the numbers okay.

See the numbers what I am giving you in this infrared spectrum they are all approximate for every compound with the same functional group it will show you the peak at the same point. But another compound with a same functional group will show you at a peak at the same point but differing slightly depending upon the molecular structure okay. For example COOH group shows a peak around 16, 40 centimeters inverse.

All carboxylic acids will show you a peak around 16, 40 but not exactly at 16, 40 because the molecular size will be different, molecule weight will be different and the environmental different like that. But there it will be around that 16, 40 centimeters inverse like that, in this case look at the slide now carbon-carbon, carbon-nitrogen, carbon-oxygen, they all appear around 19 00 to 1500 that is why the range is also slightly bigger.

Now in same way I can take a look at N-H, C-H and O-H group that appears around 3700 to 2630 even though it appears exactly same way in the same compound. But if the molecular weights are different and molecular structure is different they appear in the same range but at different places that is what you should understand. Now compare this with another IR characteristic, here I have taken oxygen and it is deuterium okay molecular weight of deuterium is twice that of hydrogen.

So oxygen-hydrogen and oxygen-deuterium, so where is the peak oxygen-deuterium is occurring at 2630 centimeters inverse okay. And that is around 13.8 microns and oxygen-hydrogen this is something like alcohol okay O-H group. So, an alcoholic group appears at 3570 centimeters inverse, so what I am trying to tell you here is if you know the structure of a compound and 1 of them is deuterium detoriated.

Then you will see 2 peaks for the deteriorated compound as well as deteriorated compound, so O-D and O-H appear differently. So, that is important as far as our studies are concern, so again coming back to the top portion of this slide bending vibrations generally requires less energy that is understood. So, they occur at longer wavelength that is understood then the stretching vibrations and stretching vibrations are also found to occur in the order of their bond strength.

So, I have here a change for carbon-carbon double bond carbon-carbon triple bond and carbon-carbon single bond, among the 3 these are bending vibrations you can see carbon-carbon single bond carbon-nitrogen, carbon-oxygen lower wavelengths. Similarly different wavelengths for different compounds and O-D, O-H different compounds like that infrared spectroscopy can be used to interpret different IR peaks for different compounds okay.

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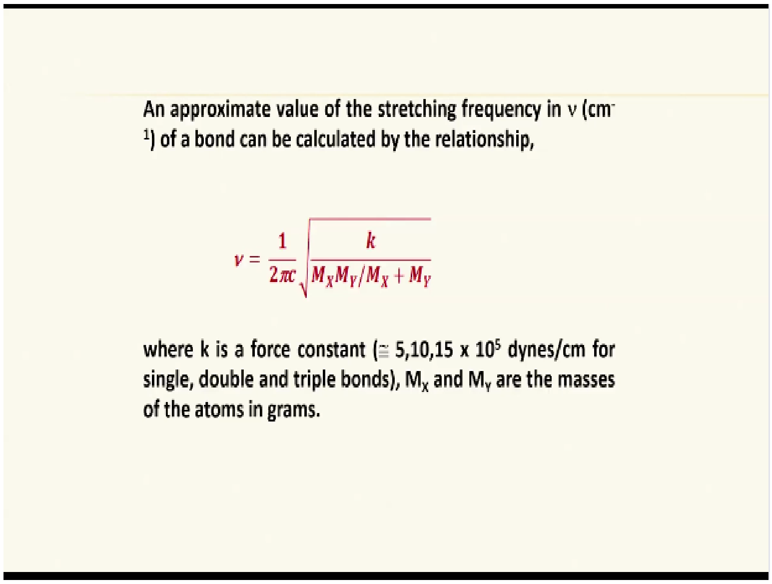

An approximate value of the stretching frequency in ν (cm^{-1}) of a bond can be calculated by the relationship,

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{M_X M_Y / M_X + M_Y}}$$

where k is a force constant ($\cong$ 5,10,15 x 10^5 dynes/cm for single, double and triple bonds), M_X and M_Y are the masses of the atoms in grams.

Now an approximate value of the stretching frequency of a bond can be calculated, this is the little bit theoretical we are not going more into the details but I want to tell you is you can calculate the where an IR peak occurs in a given system. So, the quantum mechanical calculations permit as to even if I without taking the spectrum I can determine where I can expect an IR peak.

So, that one that relation is given by mu=1 over 2 pie C*square root of k/MxMy/ that divided by Mx+My. This quantity MxMy and Mx+My, this you should remember as far as infrared spectroscopy is concerned. Because this is here you can see that k is a force constant that is approximately 5, 10, 15*10 raise to 5 dynes/centimeter for single bond it is 5*10 raise to 5 or double bond it is 10*10 raise to 5.

And triple bond it is 15*10 raise to 5 and that is k pie you know C is velocity of light mu is the frequency and Mx and My are the masses of the atoms in grams that is basically atomic weight okay. So, if it is carbon it is 12, if it is hydrogen it is 1 oxygen is 16 like that, so M the quantity MxMy/Mx+My is known as reduced mass. So this is important you should what is reduced mass and if I know the atomic weights and if I know the force constant I can predict where I get the infrared spectrum or infrared peak.

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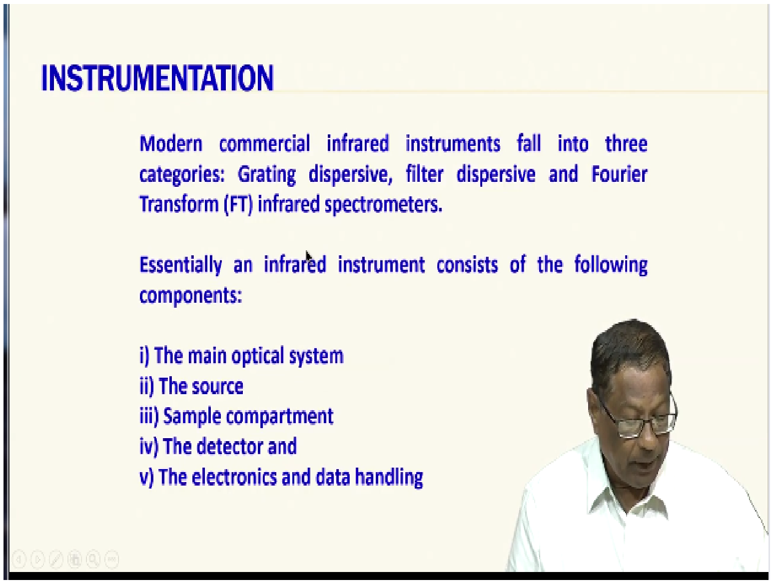

INSTRUMENTATION

Modern commercial infrared instruments fall into three categories: Grating dispersive, filter dispersive and Fourier Transform (FT) infrared spectrometers.

Essentially an infrared instrument consists of the following components:

i) The main optical system
ii) The source
iii) Sample compartment
iv) The detector and
v) The electronics and data handling

So, with this much information we will continue our discussion about the instrumentation, there are many other aspects of instrumentation. And sample handling etc. that we will study in the next coming classes, so thank you very much.