Infrared Spectroscopy for Pollution Monitoring
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Lecture-15
Infrared Instrumentation

Students greetings, we are continuing our discussion on the infrared spectroscopy, last time I have taught you about molecular vibrations, one was about the stretching and other was bending. I had shown you these slides in the last class.

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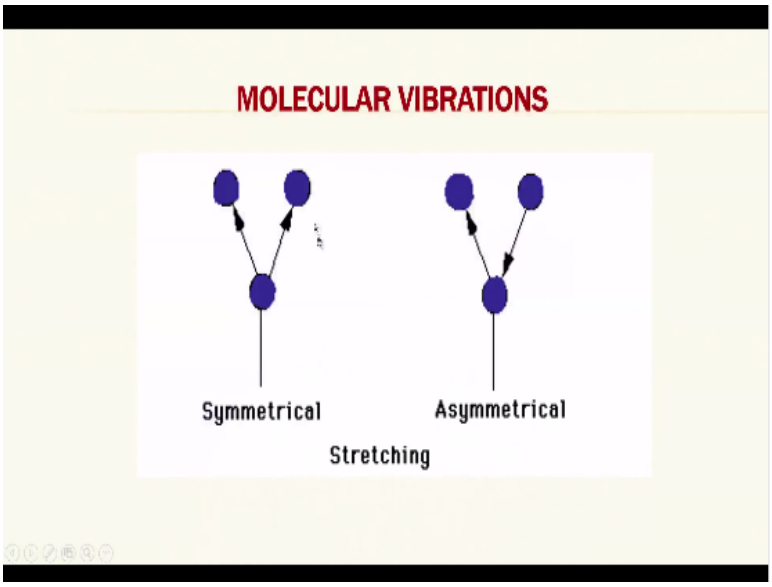

These are symmetrical stretching and asymmetrical stretching and I had shown you bending vibrations also which constitute rocking, scissoring, both being in plane deformation.

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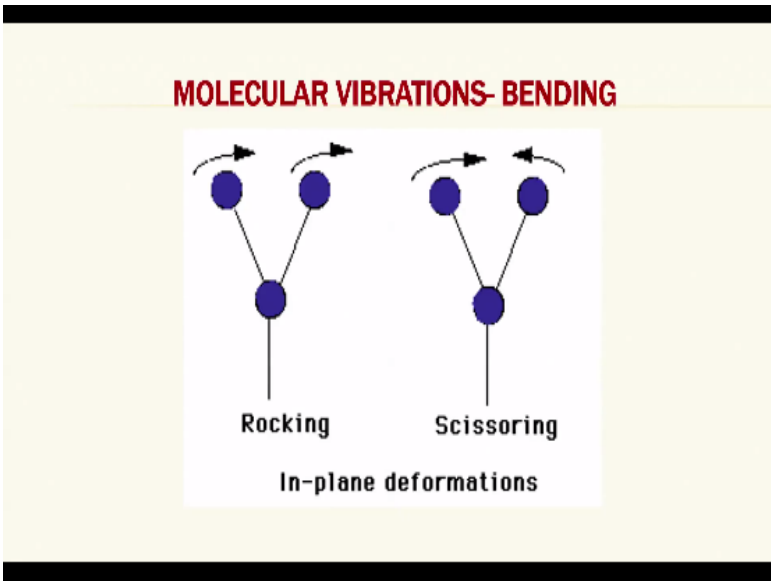

And wagging and twisting which are out of plane deformation.

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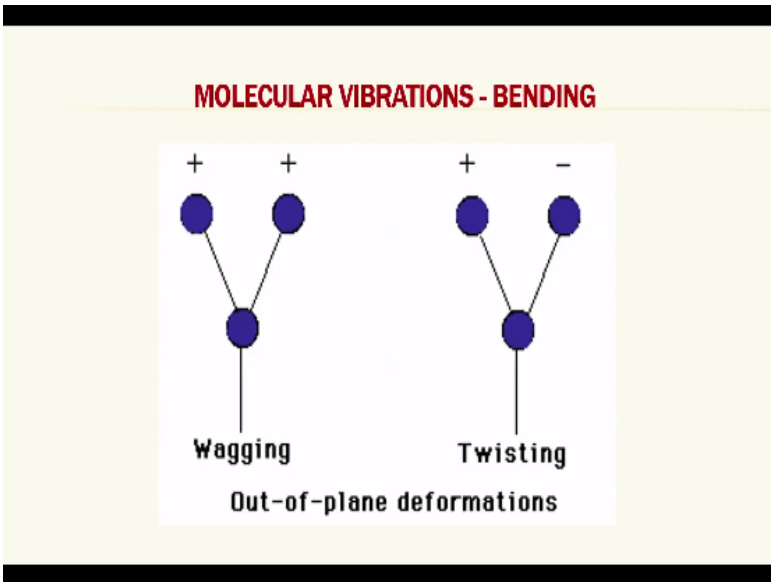

So all these things lead to infrared radiation being observed at the correct frequency of these rocking twisting, wagging and the stretching, all these frequency.

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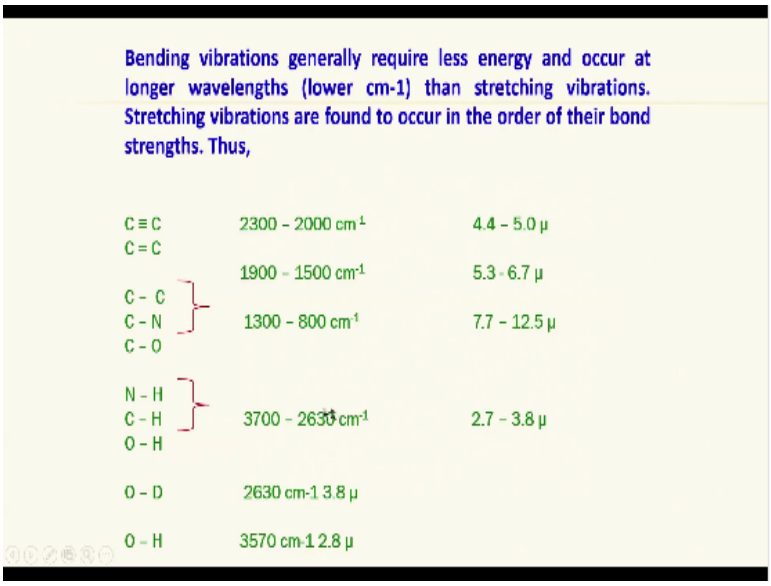

I had shown you that these bending vibrations generally require less energy and occur at longer wavelengths whereas switching frequencies are at higher energy. So if I compare a double bonded with it is triple bond I can always see that compared to a single bond double bond and triple bond stretching frequency occur at higher energy than the single bond. I had shown you this carbon-carbon, carbon nitrogen, carbon oxygen single bond stretching frequency.

Somewhere around 1300 to 800 and 1900 to 1500 and the typical stretching frequencies for double bond and triple bond are around 2300 to 2000, that range is depends upon the environment. So similarly we have compared the atomic masses for carbon nitrogen and oxygen and single bond stretching frequency with respect to hydrogen. So here what happens we see the stretching frequencies somewhere between 3700 to 2630 cm inverse.

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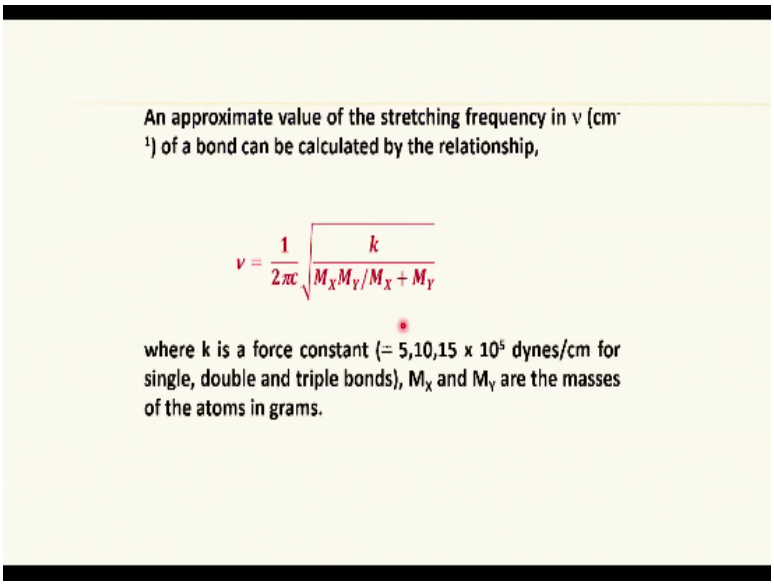

And then we have compared the doubling the mass using hydrogen and hydrogen being smaller compared to deuterium ok and the stretching frequency for hydrogen would be requiring higher energy than deuterium. So we had try to write approximate frequency whereas streatching frequency would occur and that stretching frequency is given by this equation 1/2pi and square root of k/MxMy/Mx+My and I should have told you that MxMy/Mx+My the denominator in this equation is the reduced mass.

That is one is 2 atoms are there for any bond infrared peak to occur, so the both the atoms atomic weights are mixed like this to get the reduced mass that is also called as effective mass. So I have written here when force constant k and that k there is in lines per centimeter for single bond double bond and triple bond the values vary from 5, 10 and 15*10 raise to 5 dynes per centimeter.

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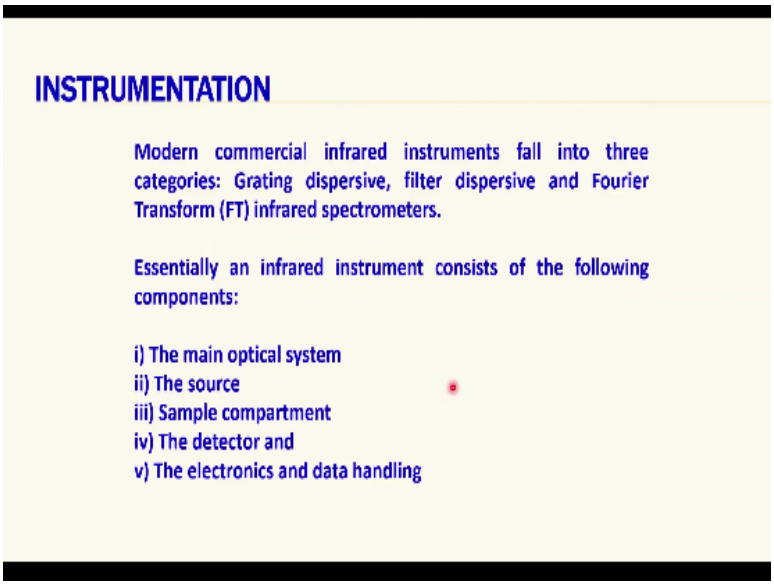

So with this we had stopped there and now I want to take you to the instrumentation of infrared spectrometer, because there are no point in going in to the theoretical details, the success of any infrared analysis depends upon the interpretation, and interpretation is again dependent upon how good your infrared spectrum is and in turn is dependent up on how good the instrument is ok.

So we have already covered various aspects of instrumentation like prism, sources etc. but for infrared we in general we know that the instrumentation has to be perfect, we know the general sources of this electromagnetic radiation etc. for infrared there is less something different. So in the instrumentation what we are going to study, how the instrument is arranged and what are the sources, how is the sample compartment organized.

The little about the detector and the electronics and data these are the 5 components and you can take a look at this slide now, the most of the modern commercial infrared spectrometers instruments fall into 3 categories, one is grating dispersive, that is we use gratings for separating the electromagnetic radiation and filtered dispersive, that is we use filters for cut off and then sometimes the we can use prism and filter combination ok.

I had explained to you about the prism Litrrow mounting, corning mounting etc. earlier in my interaction with the electromagnetic radiation. So those kinds of instruments where available

about 10 years before even now they are available and now a days the most important development in the infrared spectrum spectrometry is the Fourier transform infrared spectrometers ok. So the commercial instruments can be classified into these 3 categories.

Essentially if you want to buy an instrument best is as of now Fourier transform and next best is grating and the next best is prism. So depending up on your finances you can go for the typical instruments whichever you need but in all these instrument the essential components of the instrument will remain the same ok only the optics and mode of separation of the electromagnetic radiation is different.

That is the while scanning what you need is here to start from 4000 cm inverse to 200 cm inverse range. So how to cover this 400 to 2000 cm inverse like you know automatically. So for all these automatic instruments the unlike spectrophotometry you cannot do it manually you go from 4000 and then 4000, 3950, 3900, 3000 like that you cannot do. So the infrared peaks are so sharp that within 1 or 2 or 5 cm inverse you may miss a peak.

So 90% of the instrumentation for infrared is automatic scanning instruments. So for scanning instruments what you need is a continues step up motor which will defined at what unit the wavelength will be changing. So it may be set at 0.01 cm inverse or 0.1 cm inverse depending upon the quality of the instrument ok. So in general we can say that grating dispersive for filter prism and filter dispersive and Fourier transform.

These 3 can use essentially an instrument entire instrument would consists of the components main optical system ok that is the heart of the system I can say and next is the source, this is another important aspect of the IR spectrometry, sample compartment again it is a special compartment of which is followed by the detector and the software and quality of the spectrum is determined by the electronics and data.

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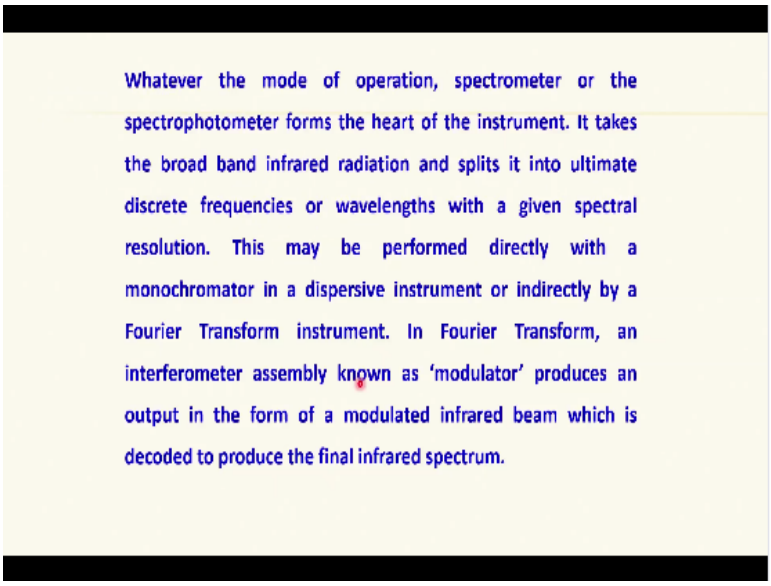

So you can say whatever is the mode of operation, spectrometer or the spectrophotometer that forms the heart of the instrument, it takes broadband radiation, infrared radiation all the way from 200 to 400 comes as a bunch ok and that is split into small, small discrete frequencies or wavelength with a given spectral resolution depending upon whether it is filter parameter or grating dispersive spectrometer.

But if it is fourier transform that is slightly different will study that also, that I will explain to you in a little while, but the grating and filter spectrometer may be the spectral resolution can be perform directly monochromator in a dispersive instrument, we can I have taught you all this monochromator, single slit, double slit etc. etc. we can go back and look at the arrangement of monochromator slits double slits arrangement and all that.

And then prisms, and then gratings all those things I have taught you. So but the scanning is usually done in a dispersive instrument and how do we do it in a Fourier transform, it is done indirectly. So in Fourier transform what to use this an interferometer assembly that is known a modulator that produces an output in the form of a modulated infrared beam which is recording decode to producing final spectrum, take a look at this slides now.

Because I am going to define exactly 2 types of instruments, one is grating dispersive but I am not going to tell you about the how it is done in grating or prism dispersive I have already taught

you but in fourier transform I am going to talk about it will have a interferometer it works on the principle of interferometry and that is a part of Physics I think most of you may be knowing from your Physics knowledge or you can just read up it is in second year physics in a second year degree physics level.

And that is we use a modulator that produces and output in the form of modulated infrared beam total. So here what happens if we use without separation all the infrared coming from a source to make it fall on the sample collect all the information and then do the separation what are the incoming what are the outgoing at each frequency can choose the frequency.

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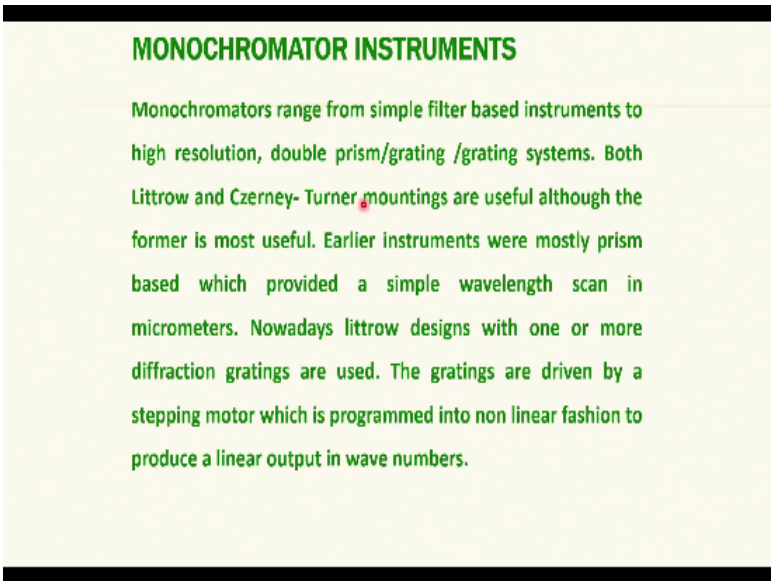

Now look at the monochromator instrument, they are all very simple instrument, take a look at the slide I have possibilities for monochromator I can make them from simple filter-based instruments. These are very early life instruments ok somewhere around 1950s and 60s IRU were based on simple filter and then they graduated to high resolution double beam and double prism and see double prism is quite often single prism is not enough to separate the IR.

So sometimes you separate visible and infrared and UV using ones prism take the infrared near infrared and infrared put one more repeat prism in the optical path, then that in the second prism will separate the infrared frequency. So the we have double prism and either you have a double

prism or I can go for grating even in grating you can change, you can look at the slide now. I have written as grating prism grating or grating rating systems.

That means I can go for just like prism, prism arrangement double prism arrangement I can go for double grating arrangement also, that is known as grating, grating arrangement ok. So I can use either Littrow or Janitor mounting, both arrangements are quite popular, so earlier instruments were mostly prism oriented base which provided a simple wavelength scan in micrometer ok.

Nowadays littrow designs with one or more diffraction gratings are used and the grating for driven by a stepping motor which is programmed into nonlinear fashion to produce a linear output in where number. This is important, see in most of the prism the separation of the electromagnetic radiation after the emission from the prism material is not uniform. So you need the split has to be moved to different places not uniformly.

But in a skewed fashion to get desired valence, they are not the spacing between the frequencies are not exactly uniform. So that stepping we need a stepping motor ok to move that slit along the emission point and that has to be programmed into nonlinear fashion. For example you may initially the frequency is a bunch together later on frequencies separate. So to go for about 5 cm, 5 cm inverse in the initial stages.

Somewhere around 4000 etc. you may have to move the slit by 0.01 mm but in the shorter range that around 200 cm they are well separated. So you may have to use 0.01 cm. So the stepper motor also needs to be moved in a nonlinear fashion, it cannot go every time 0.001, 0.008 will take long time to cover 4000 to 200 cm inverse. So a stepper motor is a very important concept infrared spectroscopy.

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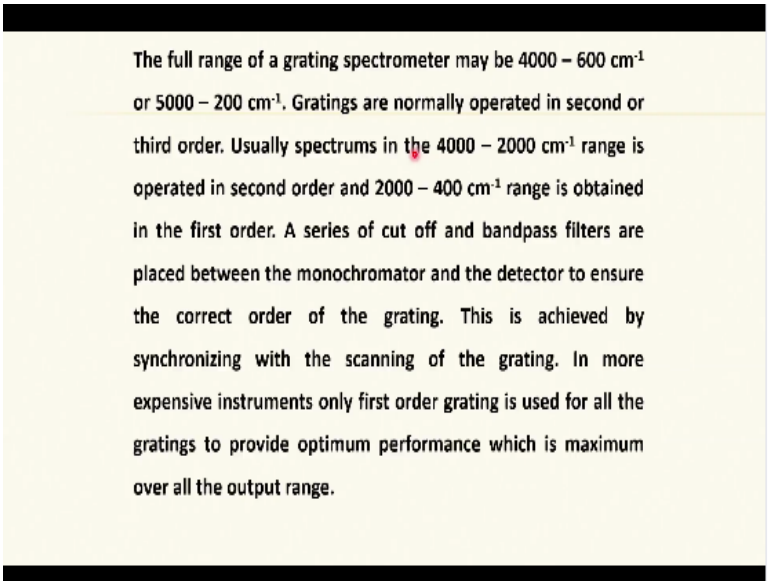

So the full range spectrophotometer that is IR it may be from 400 to 600 cm inverse which I have already told you in the first class itself or 5000 to 200 cm inverse, we can have 3000, 3000 usually people do not have 4000 to 200 is quite common. So gratings are normally operated in the second and third order not the first order. So usually spectrum in 4000 to 2000 cm range is operated in the second order.

And 2000 to 4000 centimeter is inverse range is obtained in the first order. This is what I was trying to tell you. So the idea is the 2 gratings why do we need is for this reason 4000 to 2000 range grating spectrometer at operate in the second order and 2000 to 400 cm inverse I was operating the first order. So what is the order of grating I have already taught you, we can just freshen up and for that what do I need.

I need a series of cutoff and band pass filter, this also I have taught you, they need to be placed between the monochromator and the detector to ensure the correct order of the grating. This is achieved by synchronizing the scanning and grating with a stepping motor. So in more expensive instruments only first order grating is used for all the greetings to provide optimum performance with a maximum over all the output range.

What does it mean, that means if you operate a grating in first order the intensity of the radiation what you get is much more than in the second order ok. So if you operated in the third order

intensity would be much less than the second order. So what is the preferable mode of operation, the preferable mode of operation in first order, so in modern instruments they become expensive, because first order, second order operations you need to have the post grating optics nearer the grating.

That means you may the instrument becomes very compact and it becomes costlier ok. So we need to provide optimum performance with maximum energy output over all the output range that is first order. So that is why they become very costly ok. So a grating I can use it blazed at 2 angles I know I hope you remember what is blazing, that is when I get a grating I can use a plane mirror and then keep on drawing prism or linings perpendicular ok.

Perpendicular to the glass I can draw keep on drawing different lines up to 30000 whatever is the requirement for ruling, but if I hold instead of like this if I can hold it like this the grating will is the prism what they give you what you get will not be normal to the plane but it will be at an angle like this ok towards like this. So 1, 2, 3 4 like that you will get number of prism but at an angle that is known as blazing angle.

So the greeting blaze that 2 angles first I draw it like this with 30 degree angle and then I can increasing with 90 degrees or 80 degrees or in 120 degrees like that I can have 2 different blazing's in the same grating it is as good as using to grating because the first part will give you the dispersion in one area and the second part will give a dispersion in the 4000 to 200 or something to 200 or something 2000 to 200 range ok.

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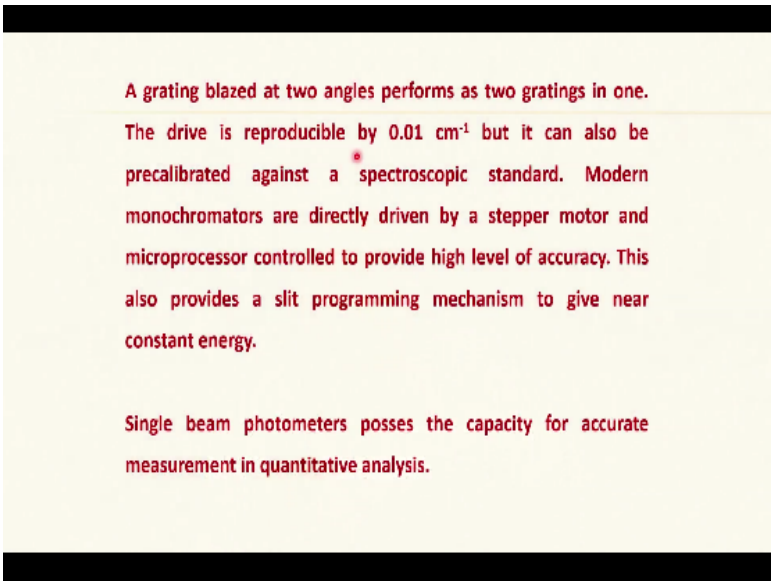

So the drive in such greetings is reproducible by 0.01 cm inverse accuracy. So what are we talking about we are talking about accuracy of the infrared radiation scanning should be +/-0.01 cm inverse in which the graph is drawn. So it can also be pre calibrated against spectroscopic standard see generally what happens is whenever a grating is to be drawn I would it is impossible to produce a grating by ruling every time.

It is a big engineering job, so what people do if they produce one master grating and on that they superimpose transparent polyester resin and then take off the polyester resin that will give the duplicate of the of the grating ok, such things can be mass produced that means with one single master ruler grating you can produce 100s and 1000s of the replica gratings and these replica gratings are cheaper because they are all made of polyester.

And all the deed is a little bit of a resins to be placed on the on the grating with a separating agent and once the result is set you just separate the 2 components your master grating you will get it back and you are grating in to be used in the instrument would be a resin grating which is cheaper than the original. So such things need to be standardized against a spectroscopic standard with respect to the accuracy of the wavelength ok.

So modern monochromator are normally driven by stepper motor that I have already told you and these are all microprocessor controlled. Now a days electronics has grown up to such an

extent that the accuracy obtainable in infrared is almost of the order of 0.001 but then again if you want to scan at 0.001 cm inverse to cover from 4000 to 200 cm inverse will take about 2 hours, 3 hours even not want that to take an IR spectrum.

So it is a compromise the scanning should be as accurate as possible, date should not be lost as much as possible. So you had a make a compromise 0.01, 0.02 and 0.05 cm inverse scanning speed to cover 400 4000 to 2000 cm inverse infrared range. So that is governed by a stepper motor and a microprocessor control ed to provide high level of accuracy. So this also provide a slit programming mechanism.

Because we have to move the slit also that is to be synchronized to give near constant energy. So single beam we have single beam spectrometer as well as double beam spectrometer. They possess the capacity for accurate measurement that is no distortion of the IR and they are more energy output, so sharper IR peak changes. So single beam infrared photometer they are better than double beam.

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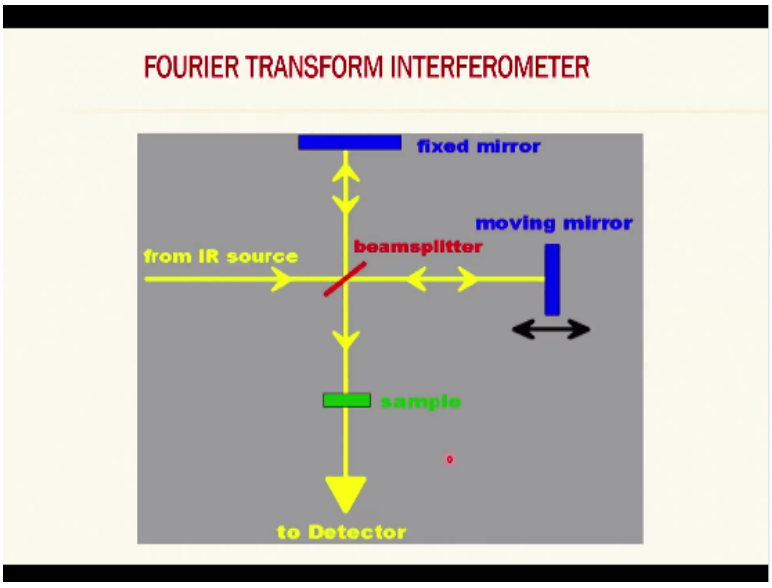

Because in double beam energy is split into 50, 50. So the quality of the IR will be match less ok. Now we will talk about Fourier transform interferometer, so far what to have talked is about the optical system of a spectrometer infrared spectrometer ok. Now in optical spectrometer I had told

you that filter photometer prism and cutoff filters, monochromatic band filters and then other things. Second is grating, grating, blazed holographic grating and all those things.

Now I am coming to the third part of the optics that is instrument itself is different and this is special right now the 90% of infrared spectrometer being produced are having Fourier transform IR spectrometry. They are called as FT-IR, FT-IR spectrometers and what is so special about it, the only thing special about fourier transform IR is the optical system nothing else remaining part the source and then sample compartment all other things remain the same ok.

So far we have discussed about the optics, now we are going to discuss about the optics of the FT-IR ok. So what is FT-IR, Fourier transform interferometer, so it is essentially mirror range arrangement ok. Here is the radiation coming from infrared source, I have not taught you about it yet, you see from here ok, I kept a source somewhere here, the radiation comes like this and then I have a beam splitter ok.

What does this beam splitter do, it cuts the infrared radiation into 50% part of it goes directly through on the same optical path and the remaining part is going vertically, that is at 90 degrees to the transmitting. So here I have fixed 2 mirrors one is this one is a mirror, this is a moving mirror. That means this mirror move like this look at my pointer it moves only this much distance ok, maximum minimum, minimum maximum ok.

Here I have one more mirror, this mirror is fixed that means it does not move, so the whole arrangement of infrared spectrum FT-IR involves in making the infrared source divided into 2 parts and 1 part is goes here, goes to the moving mirror, it hits it and then gets reflected then the same way and then comes to the beam splitter and comes back ok. And the remaining 50% goes to the fixed mirror and it comes out like this again in the same path passes through this midpoint.

And then both of them are combined and then again allowed to fall on the sample and of that means all the radiation from the source is allowed to fall on the sample without any optical separation and then after the sample all the radiation is collected except that part which is not observed by the which is observed by the same sample. So what I am trying to do essentially is I

am taking all the radiation that is coming out it cut 50, 50 like this when first part goes to a moving mirror.

I introduce that means it is a small aberration in the optical path because the mirror is not constant ok, this moving mirror this one ok. This mirror but this is constant, so I have 2 beams differing units distance between the reflection reflected beams and then they are re combined. So the aberration as well as original beams are connected collected through the beam splitter and this beam splitter will take all the radiation into the sample part of it is observed remaining part is not observed.

And what is not remaining is allowed to be collected on the detector. This is all the optical arrangement of the FT-IR spectrometer. So what is so special about FT-IR at all, now there comes the beauty for that you have to understand a little bit about the theory of spectrophotometer the FT-IR that we will study in the next session.