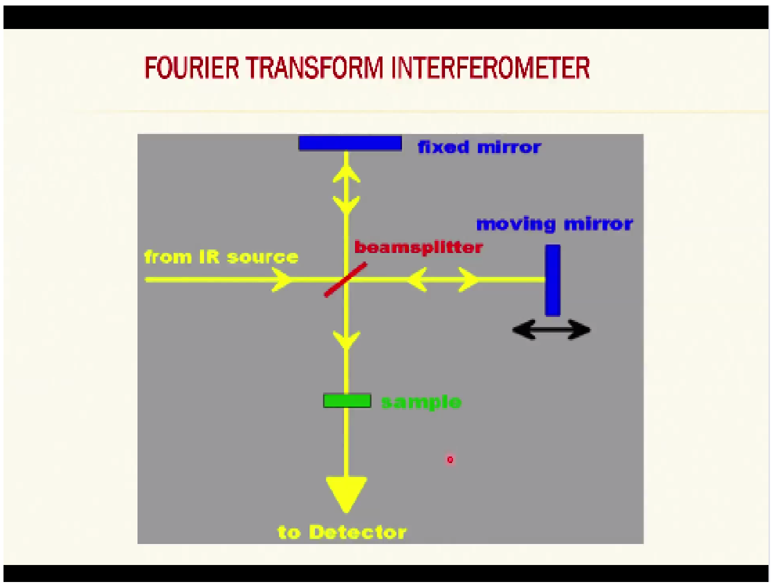
Infrared Spectroscopy for Pollution Monitoring
Prof. J.R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science-Bangalore

Lecture-16
Fourier Transform Infrared Spectroscopy

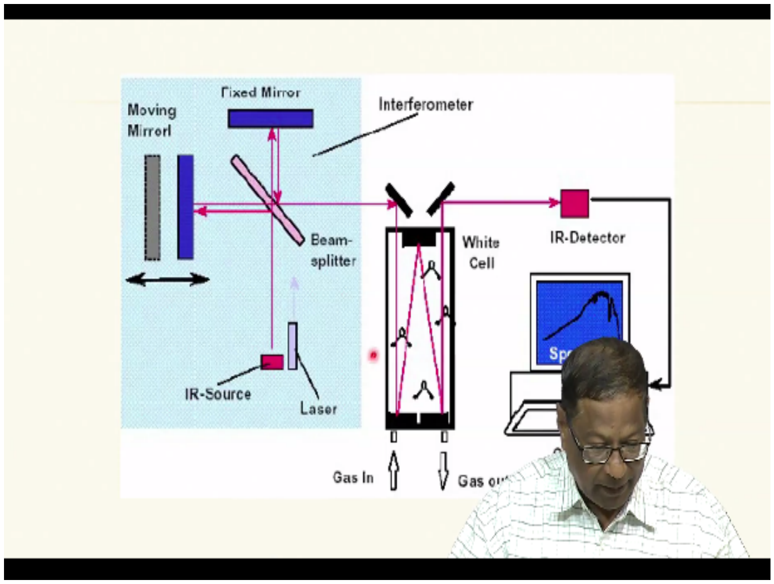
Hello everyone, so I have been showing you this picture in the last class we close there.

(Refer Slide Time: 00:21)



IR source I have been splitter, I have moving mirror, I have fixed mirror, beam splitter splits into 2 and then fix a mirror reflects, the moving mirror also reflect. All the reflected radiation is passing through the sample and goes to the detector whatever is the remaining that is on except IR.

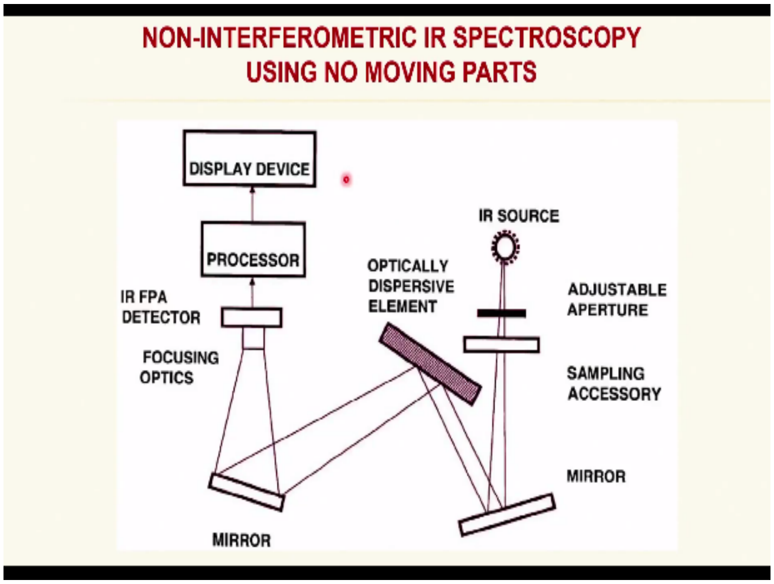
(Refer Slide Time: 00:46)



So the arrangement is something like this ok, so the whole instrument that is FT-IR instrument arrangement is like this I have an IR source here ok and I have a laser here that also passes through laser is only a reference beam to standardize the IR ok. So that also passes through and the beam splitter is here, moving mirror this way fixed mirror and then this is known as interferometer ok.

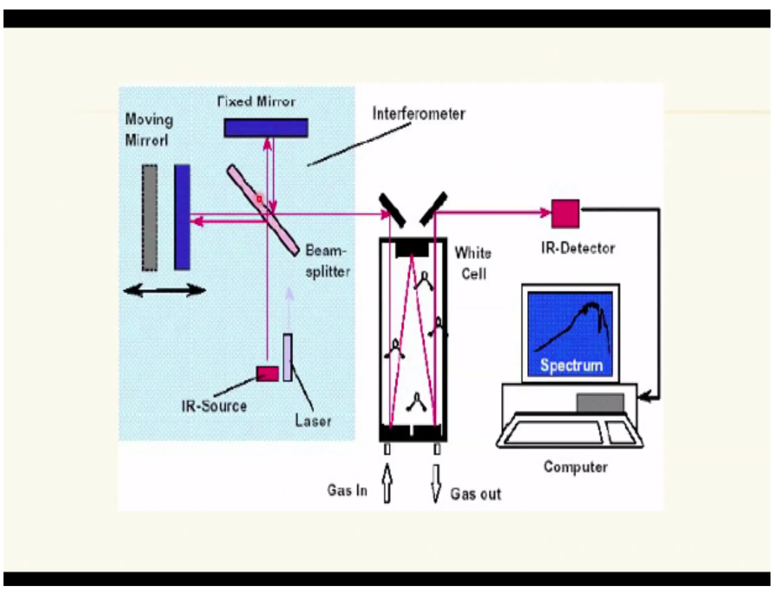
And they both are combined and I have a mirror here again maybe a concave mirror and then it comes down like this, and then one more, then here, then out, this is the sample compartment, there is some gas coming in and gas going out ok and the IR detector is here and this is a computer that controls everything. That is movement of the moving mirror and then laser control and then reference control and then sample collection of the data and all that ok.

(Refer Slide Time: 02:24)



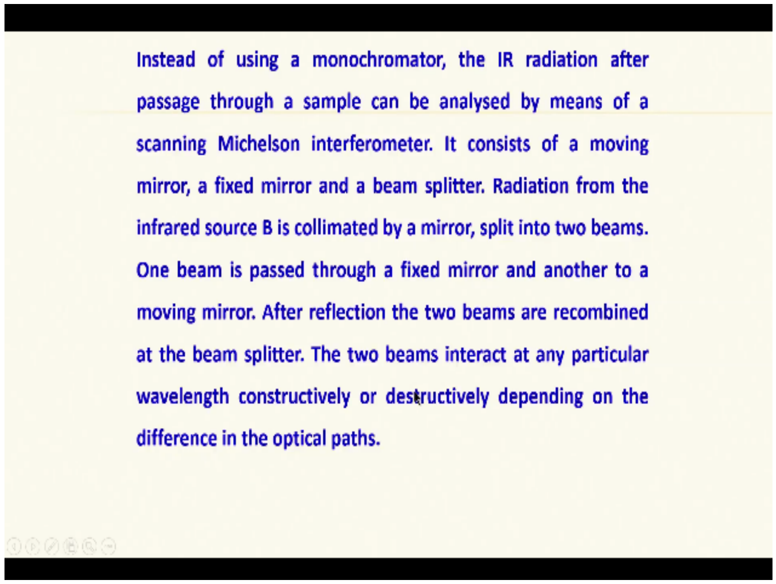
And it producers a IR spectrum here, so non interferometric IR spectroscopy, this is the typical optical arrangement ok I have IR source here and then adjustable aperture is basically a split is and then a sampling accessory, I have a mirror and this is the grating, this is non FT-IR. So grating is here and all the radiation from the grating is collected on to the mirror and it is focused and then IR-FPA detector is here.

(Refer Slide Time: 03:18)



After the detector I have a processor and a display device that is a monitor essentially ok. So the previous one is FT-IR and this one is normal IR ok.

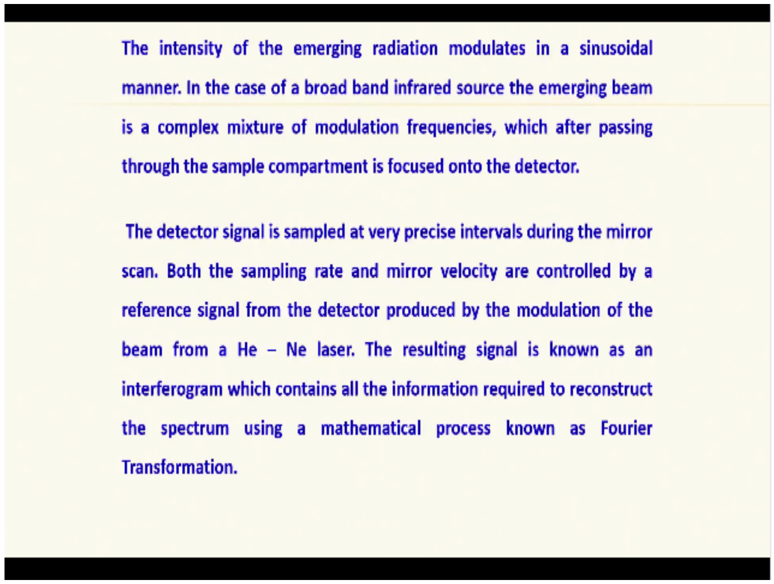
(Refer Slide Time: 03:25)



So instead of using monochromator the IR radiation after that passage through a sample can be analyzed by means of a scanning Michelson interferometer. This is a sort of again second year PU physics material that is interferometer they start around that level, basically it consists of a fixed mirror, moving mirror, beam splitter etc. So radiation from the infrared source is collimated by a medicine already told. I have only putting it here for the record.

So that you will know exactly what is happening, so the mirror is split into 2 beams one is passed through fixing mirror otherwise removing mirror after reflection the 2 beams are the recombined and they interact at any particular wavelength constructively or destructively depending upon the difference in the optical path. Now this optical path is introduced because of the moving mirror ok.

(Refer Slide Time: 04:34)

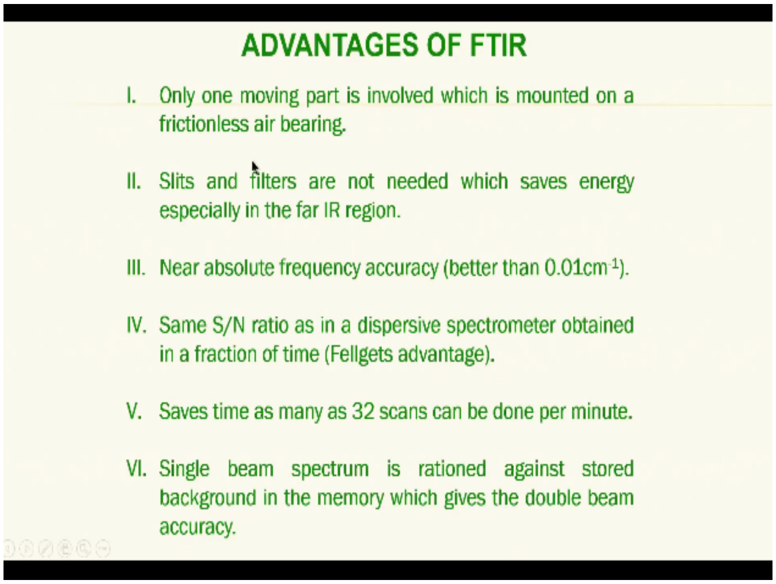


So the intensity of the emerging radiation modulates in a sinusoidal manner that is in a repetitive management, in the case of broad band infrared source the emerging beam is a complex mixture of modulation frequency, all of it slightly different slightly by because of the moving mirror, everything is focused on to the IR. So this passes through the sample compartment and then on to the detector.

So the detector signal is sampled at very precise intervals during the mirror scan, when the mirror is moving ok at that time a very precise moment of the mirror of the order of work maybe. 0.1, 0.01 mm is it is kind of like that. So both these sampling rate and the mirror velocity are controlled by reference signal from the detector that is the laser pointer at the laser light that I had shown in the second picture.

So that is produced by the modulation of the beam from a Helium neon laser**.** So the resulting signal is known as interferogram. So what is the interferogram, it is the total radiation coming out from the infrared source after it passes through the center or every information all the wavelengths differing only slightly by a little bit of moving mirror changes.

(Refer Slide Time: 06:46)



So it contains all the information required to reconstruct the spectrum using a mathematical process known as Fourier transform transformation Fourier transformation it is a very well-known mechanical scheme. I am not going into details of what is a fourier transform and what is a fourier equation etc. they are all taught at B.Sc level fourier equation, fourier transfer equation is basically an infinite series and the question I will actually question I can present it to in the next class but basically it is a non ending series continuous infinite series ok.

1+x bar 1/1 then x square/2 factor then x square by 2 factorial and x cube three factory something like that it keeps on going and maybe having it here in my slide but let me show it in the next slide exactly what it is ok. Now assume that basically what we are having is just like an infinite for fourier mathematical expression which contains all the related number. I have all the related numbers of an electromagnetic radiation from IR ok coming through the mirror.

So it is something equivalent to FT-IR fourier transform equation, so what are the advantages of FT-IR over the normal filter photometer or grating rating photometer I have listed them here and we can see there is only one moving part that is involved which is mounted on a frictionless bearing air bearing. For example I am going back again a little bit yeah this moving mirror is mounted on a frictionless bearing.

That means the movement of this mirror is very smooth because it is controlled only by air movement you air bearings and it is uniform it is reproducible at etc. etc. that means the movement of the mirror are exactly controlled every time you operate number an instrument ok. So that is number 1. Number 2 slits and filters are not needed in FT-IR because I do not have to sample a small portion of the electromagnetic radiation corresponding to near IR.

You know far IR nothing like that whatever infrared radiation the source throws I am collecting everything. So I do not need slits, I do not need filter. Now what does it mean that means no energy is lost, the quality of the spectrum is not lost because the light intensity falling on the on the sample and on the detector is essentially same throughout the wavelength range ok that is second advantage.

Third advantages is near absolute accurate frequency better than 0.01 cm inverse because they are all frictionless air bearing controlled by laser and also it is controlled by many microprocessor ok. So what happens is if this kind of accuracy is available the next advantage is the signal to noise ratio as in a dispersive spectrum obtained in a fraction of time, the same ratio of the signal to noise you know what is signal.

You know what is noise, you do not know, I have to explain you, so the peak in a in an IR is known as signal, the intensity of the peak below its base is known as noise ok. So basically a peak contains noise+signal. So for proper measurement noise should be as less as possible, the noise comes from electrical component ok, it is a continuous disturbance of the signal, continuous but fixed. So that is noise.

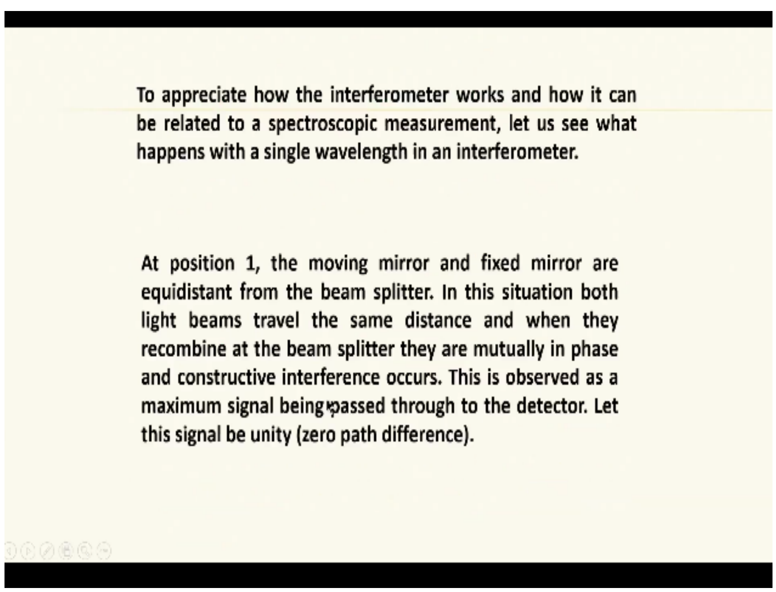
I too talk to you about noise electrical noise in any instrument separately on a separate instrumentation that I have already thought in atomic absorption spectrometry and spectrophotometry. I am not going into details of that because I assume that you know about it or you can go through them in the same NPTEL program. So the signal to noise ratio should be as high as possible that means nice should be as low as possible signal should be as high as possible.

This is obtained in a small fraction of a time, that means the noise does not very much it is already obtained and already subtracted and taken care of factor. So it says time because if I can move the mirror number of times here I have written 32 scans it saves time permanent within 1 minute I am getting all the information instead of if I know the spectrometer 0.01 cm/movement from 4000 to 200 how much time is required you can calculate per second 0.01 4000.

And then -4000, -0.01, that is 1x second 4000-0.02 next second like that but here I can be done in 1 minute, I can do that as many as 32 time scanning. So I can average it out and that is another advantage and then a single beam spectrum is ratio against stored background in the memory which gives double beam accuracy. That means in double beam what happens is I use only 50% of the radiation passing through the sample remaining without passing through the sample.

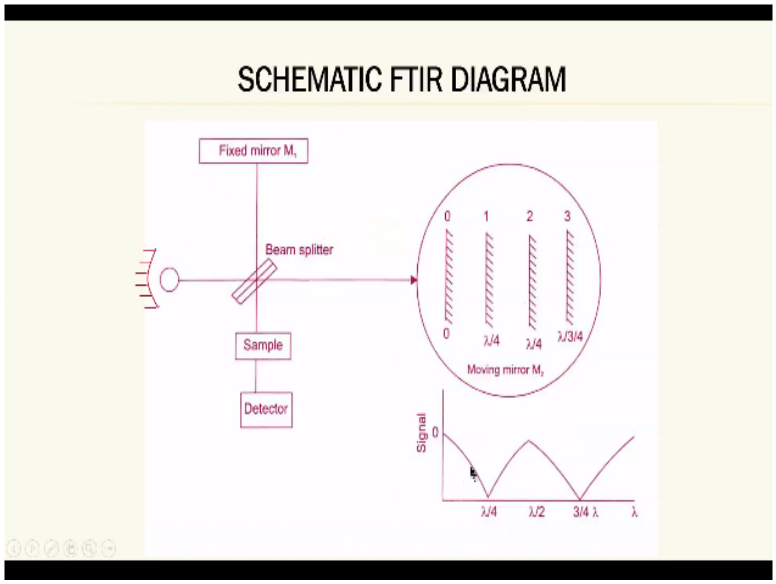
So that I can compare the ratio of the sample to that of an untreated sample. So I use only 50% of the sample for the measurement, but in single beam instrument all the radiation is passed through the sample so there because it would remain much better. So these are the advantages of FT-IR, I think you should remember all this because I will be asking you questions in the examination about these things if you are taking an examination ok.

(Refer Slide Time: 14:17)



Now to appreciate how an interferometer works, so far I told you what is interferometer and what are the arrangements etc. but how does it work I had just given you a small introduction about what is fourier equation. Now how a fourier interferometer works and how it can be related to spectroscopic measurement I told you that both of them are somewhat similar but how similarity are they. So let us see what happens in a single wavelength in the interferometer ok and I assume that I am passing only one wavelength through the source and onto the beam splitter.

(Refer Slide Time: 15:18)



And that 1 single wavelength intensity 50% goes to the fixed mirror 50% goes to the moving mirror, now assume that and then I want to show you this picture FT-IR diagram here is the fixed mirror and here is the moving mirror. The moving mirror starts from this point to this point ok. And beam splitter is here sample is here detector is here signal is here ok. Now here I have mark position 0 here it is 0, 1, 2, and 3.

Actually I can mark any number I can divide this moment of the mirror moving mirror I had divided it by 4, I but I can do it by 100 also no because it is only a theoretical or hypothetical division of the distance to which the mirror moves from this end to this end. The after it reaches here again it will start moving this side to side. So it is continuous movement of the mirror ok. So I have mark them 0, 1, 2 and 3 only for the sake of our discussion ok.

Now the position 1 the moving mirror and fixing mirror are equidistant from the beam splitter. So that means this distance and this distance actually it is not looking like that in the diagram, but you can assume that this distance between fixed mirror and beam splitter and the moving the 0 position and this beam splitter are exactly same ok. This is only a schematic diagrams, so I have not shown you.

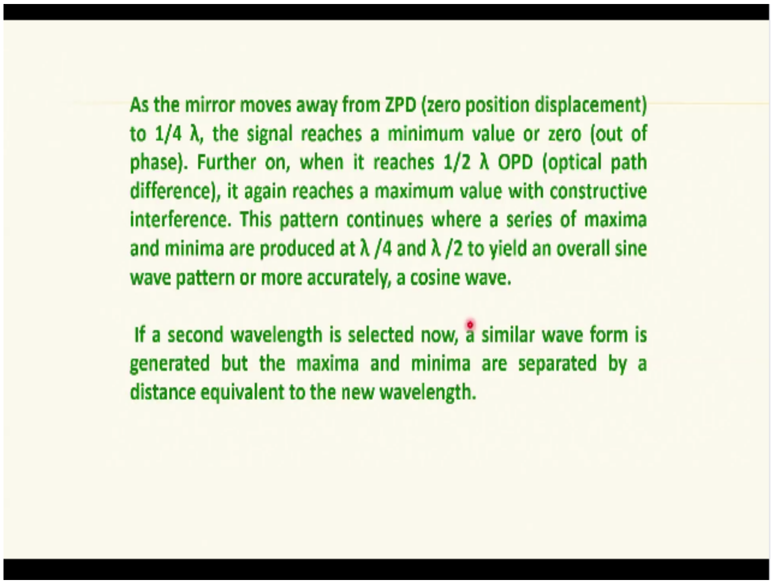
But position one is that, position in this situation both light beams travel the same distance and when the recombine the beam splitter they are mutually in face that means there is no difference between the intensity of the radiation between this position and this position ok 1 and 2. Two is always fixed mirror ok. So when they recombine the beam splitter they are mutually in the face and there is no there is only a constructive interference there in face.

Again Basic Physics I will not going into details, so that means if I have if you remember what I had taught you, you get intends bands of intense radiation dark spot, bright spot, dark spot, bright spot like that. So when they are 0 you get bright spot and when they are not 0 you get a dark spot. So this is observed as a maximum signal being passed through to the detector or it has been passed through to the detector maximum signal.

So any other position apart from this 0 position would be allowing the total radiation passing through the beams player passing through the beam splitter would be less than 0 position except 0 zero is maximum and position at 1, 2, 3, this intensity would be much less than the zero position, that is what do you mean ok. So this is observed the when it is zero what that means when both the parts are equal its observed as a maximum signal pass ok, it is being passes through the detector.

So this signal let it be unity, that is it is known as zero path difference and path difference between this and this is zero ok, then comes first position here I have latest I have moved it one wavelength remember you have taken only one wavelength, so lambda/4amplitude and taking, it has the mirror has moved here and there that means the distance between this and this is increased by this much ok, look at my pointer.

(Refer Slide Time: 20:09)

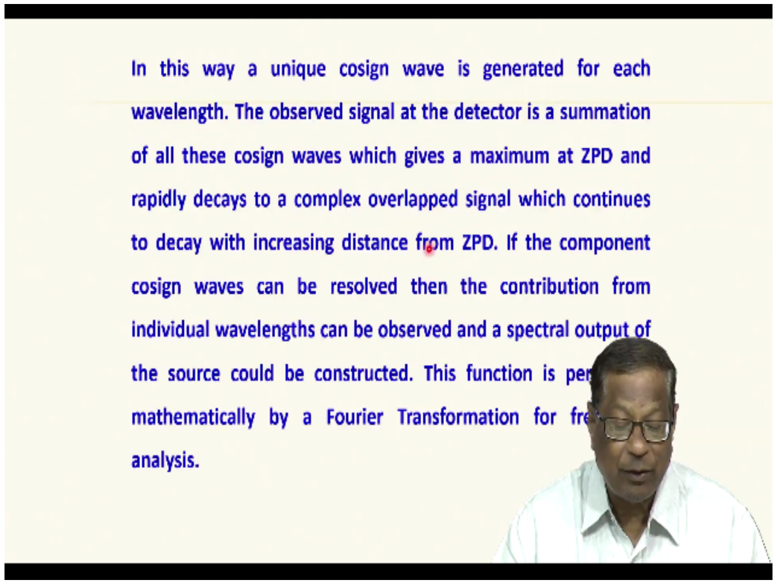


So here 0 signal and then it keeps on decreasing when it comes to lambda/4 the interference is complete and there is no signal ok right. So now as the mirror moves away from zero position displacement to 1.4 signal reaches a minimum value or zero that means it is out of phase ok, here at lambda/4 this signal reaches minimum. So here it is no signal now further or it moves it reaches 1/2 lambda OPD, what is OPD, optical path difference.

And it again reaches slowly it keeps on increasing it reaches maximum, this is at lambda/2, then again it reaches 1/4 lambda/4 it becomes 0 again lambda3/4 again it reaches maximum. So like that it keeps on moving, like this for this wavelength. Now choose the radiation coming from the IR source contains not just 1 wavelength but the number of wavelength from 4000 to 200 cm. Every wavelength goes through this process.

And all the information is obtained in 1 shot ok. So if a second wavelength is selected now a similar waveform is generated but the maxima and minima separated by a distance equal to the new wavelength ok 4000 let me say I want to check at 3999 then at 3999 again I get a maximum signal but the maxima and minima will be slightly lower than 4000 ok. So they are separated by distance it is not the quantity, it is not the magnitude.

(Refer Slide Time: 22:20)

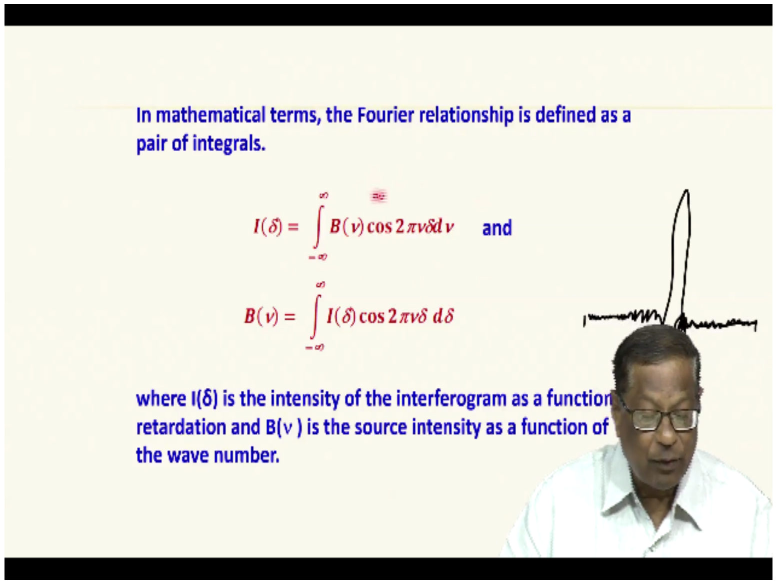


So the magnitude will remain the same ok, so in this way what happens if I will get a unique cosin wave;. For example this one is cosine wave, cosine 0 is maximum 1, cosine 90 is 0, 180 is 1, cosine 270 is 0, like that this is basically a sin wave or cosin wave. But this is cosin wave this is a high school mathematics ok. So a unique cosin wave is generated for each wavelength the observe signal at the detector is a summation of all these maxima of the cosin waves.

Then that is maximum at zero path difference that is at position 1 and rapidly DK is slowly to 0, so it indicate to a complex overlapped signal which continues to DK with increasing distance to ZPD, when the cosine waves can be resolved then the contribution from individual wavelength if I resolve all the 4000 into individual components ok. Then I need I will get it each what I get to know what happens at each individual wavelength whether it is absurd or not how much is that all how much is not absorb.

Then I can draw a picture of the spectrum, so a spectral output of the source can I can reconstruct mathematically and how I convert that mathematically converted spectrum into actual IR spectrum is done by the instrument microprocessor etc. There are various states available. This function is performed mathematically by fourier transformation technology and for frequency analysis by both of them are similar.

(Refer Slide Time: 24:33)

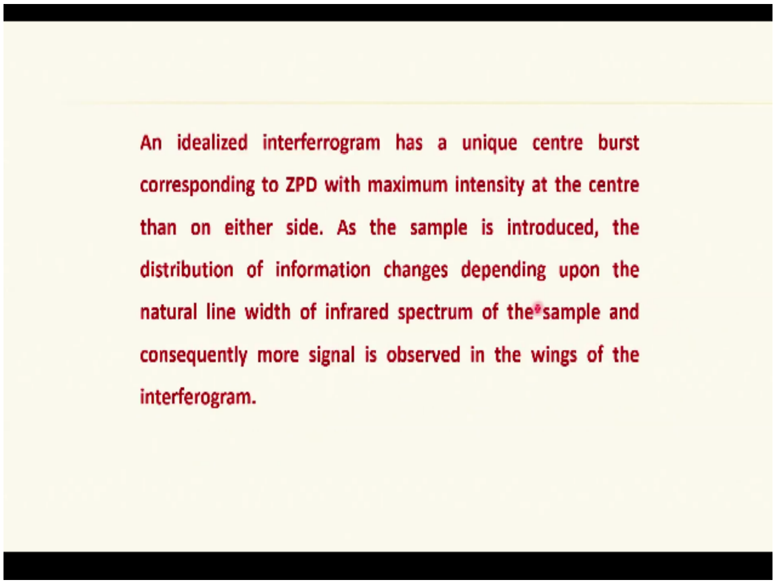


Now again I had to take you through a little bit of mathematics ok not very may not too much but a little bit bear with me. So in mathematical terms the fourier relationship is defined as a pair of integral whole for a fourier relationship I can define by 2 integrals intensity parts. One is the intensity part, another is the source intensity, one is source intensity of the interferogram as a function of retardation.

The moment of the mirror is known as retardation ok, that you should remember. So the one is intensity of the interferogram as a function of read as the movement lambda/4, lambda/2, lambda/3, Lambda/4, 3/4 lambda, like that that is I delta and another is Bv B is the source intensity as a function of the wave number. So what is at I delta, I delta is it is the intensity of the interferogram varies from -infinity to +infinity it is a signal infinite.

You know it is the infinite series and that is given by Bv*cosine wave and the amplitude of the cosine wave is given by 2piV*delta D*v and Bv is nothing but I delta, this is the both of them are functions of each other. Now you can see here, I delta is a function of Bv and Bv is the function of a I delta. So remaining is essentially same, but both of them are –infinity to +infinity. So essentially what we are saying we are saying intensity of the interferogram is almost same as intensity of resource.

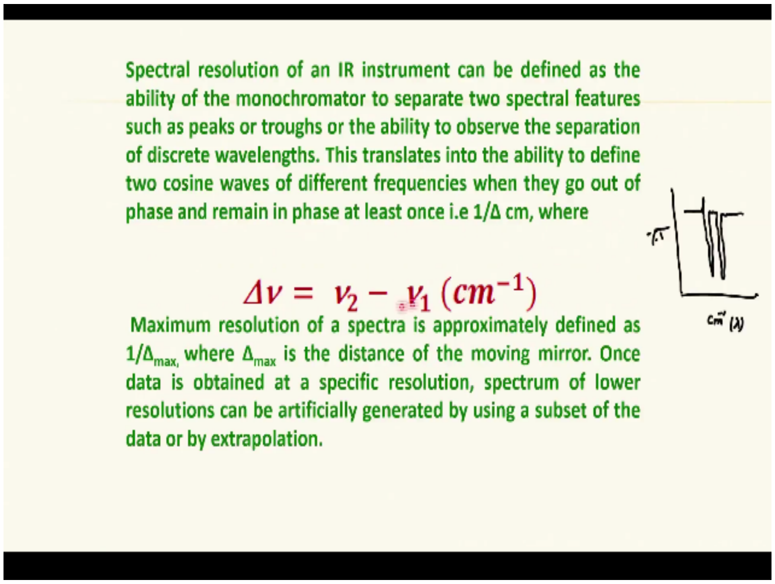
(Refer Slide Time: 27:05)



So I get 2 series of the 2 functions interdependent upon each other that is all it means basically ok. So the idealized interferogram that is 1 signal single signal what you get in FT-IR is 1 big bust maximum and then slowly decomposition it into 0. It is like plotting bell the sound of a bell you hit at once rimmmm and then slowly it goes down to imm imm 0. So like that interferogram also can be plotted like that an idealized interferogram has a unique centre burst corresponding to zero path difference with a maximum intensity at the centre.

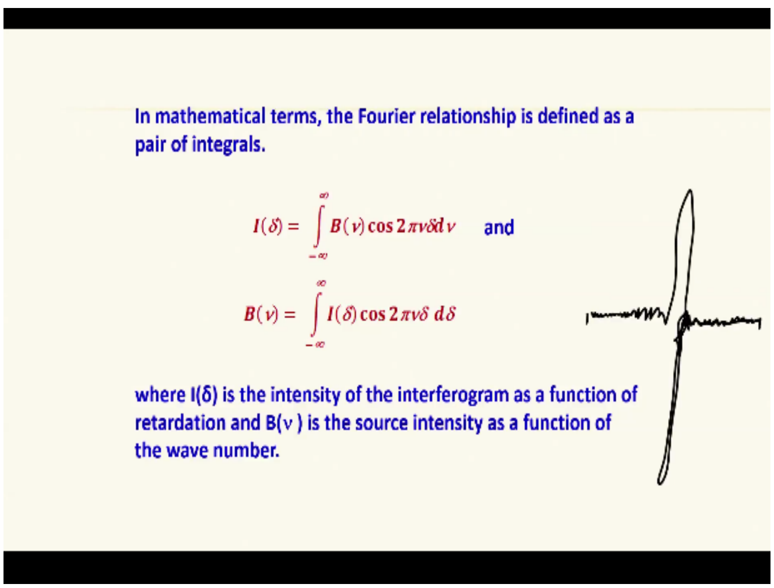
Then on either side ok, so as the centre is introduced the distribution of information changes depending upon the natural line what we have every 0.01 cm the information change and that line width of the infrared spectrum of the sample and consequently the signal also will change ok. So that will be observed in the wings of the interferogram, the actual infrared spectrum is observed at the wings of the interferogram.

(Refer Slide Time: 28:36)



Now I will show you what is how and interferogram looks as a far here I have I am not putting here, but next time I will show you that it should have been here, yes I will introduce you to that, but basically I can show you it will be like this something like this.

(Refer Slide Time: 29:14)

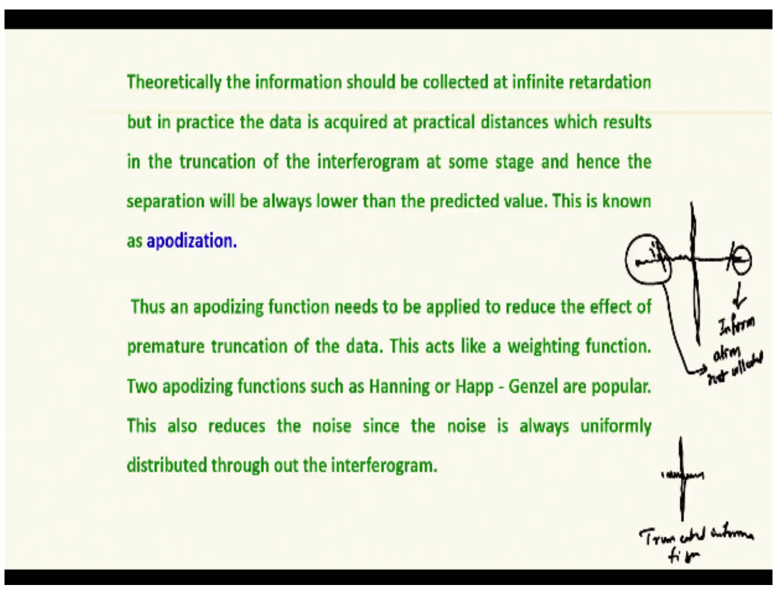


It would not be such a big gap but it will be in something like this the interferogram if centre burst and then there is something like this though. So up to this it is the interferogram ok. So the idealized interferogram has a unique centre but still like what I had shown you here and then corresponding to ZPD this I already covered. Now you know how and interferogram looks and the spectral resolution of an IR instrument we can define it has the ability of the monochromator to separate 2 spectral features such as features such as peaks or truck or as they are the ability to observe the separation of discrete wavelength.

For example if I have to draw the IR spectrum would be like this now, this is a percentage transmittance, this is the cm inverse ok, this is the wavelength for cm inverse. The 2 spectrum the how good they are separated that is what it means a delta B the ability to define 2 cosine waves of different frequencies when they go out of phase and remaining phase at least once that is delta v=v2 bar-v1 cm inverse.

And maximum resolution of the spectra is define as 1/lambda delta lambda max1/delta max where delta max is the distance of the moving mirror. So once data is obtained in that specific resolution spectrum of resolution can be artificially generated by using a subset of the data or extrapolation.

(Refer Slide Time: 31:33)



How that interferogram can be divided into small portions ok and then converted into spectrum. So the spectrum can we converted if I use detransformation ok, first I have the fourier transform spectrum, now when I do this detransformation I get the IR spectra. So theoretically the information of FT-IR should be collected at infinite retardation ok. So please try to understand now.

And a finite retardation means the moving mirror should be moving in very small and infinite speed ok, that means from one point to another point it mistake infinite time to reach theoretical, but in practice what is required is it is acquired at that practical distances ok. So I can say 1 cm maximum it can move or 2 centimeter, but if I keep it infinite distance FT-IR spectrum cannot be taken ok or it will never ended.

So I have certain restrictions, that is it is acquired at practical distances which results in the truncation of the interferogram. So now if I have a spectrum like this now somewhere here I have to cut, the rest of the information even though it may be there but I am not going to connect this information not collected, same thing is here, that means I am truncating the fourier transform to infinite to a particular finite position ok.

So this results in the truncation of the information, so truncated information is only this much, this is truncated information ok, so at some state I had to cut it off and hence the separation will be always lower than the predicted value. This is understood now, so this is known as apodization. So this truncation is decided by the manufacturer, so what is the required to be done is that I have while doing the FT-IR must say you stop at this page of the moving mirror.

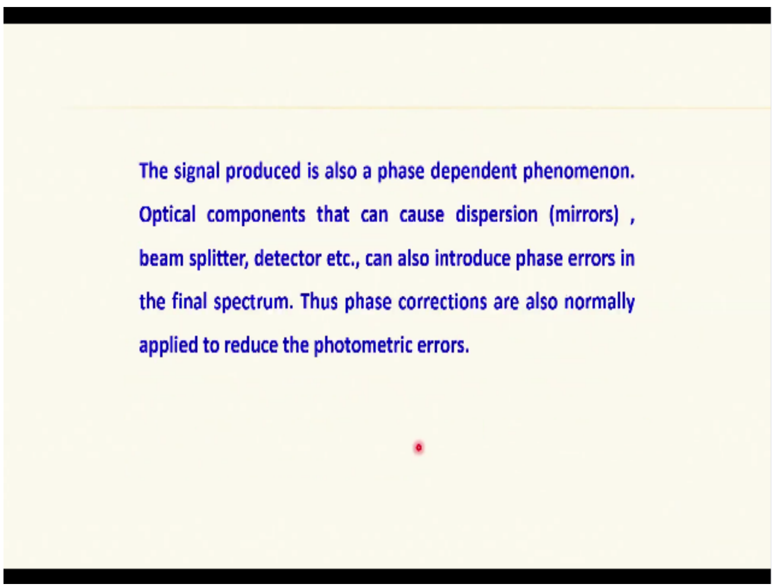
Do not make it infinite but stop after 2 minutes or 3 minutes or 5 minutes like that collect all the information within that time, so that is one truncation on either side, so this app that is known as apodization function it is done mathematically. So I can give any number I can write it in program computer program and say truncation at this level. So an apodizing function needs to be apply to reduce the effect of premature truncation.

So now you understand try to understand whenever I have to do this truncation part of the information is lost but so to take care of that I have to add a little bit of correction but how much is lost I do not know, so that function is also decided that I have to add a little bit of the information to reduce the effect of truncation, the premature truncation, that is apodization. So this act like a waiting function.

So I need 1 apodizing function on the higher frequency side, another apodization on the lower upper frequency side and then there are 2 apodizing functions you know apodizing is a separate branch by itself that is how much to cut etc. that is 2 applications are not in the instrumentation world 1 is known as hanging apodizing, another is Happ-Genzel apodization. So these 2 techniques are used for truncating the fourier transform signal.

So **so** I am not going into details of this hanging and Happ-Genzel techniques but suffice it to say that you can come you can about you can stop the fourier transform from infinite to a particular size practical size and they are known as a truncating the FT-IR fourier transform and this truncated information needs to be taken care of so that act like a waiting function and these waiting functions are known as hanging function or Happ-Genzel.

(Refer Slide Time: 38:04)



So this also reduces the noise and since the noise is always uniformly distributed throughout our interferogram. So the signal produced is also a phase dependent phenomena ok, that is understood now because I have to cut off the signal collect all the information, cut the FT-IR into specific information and then optical components can also cause dispersion that is mirror etc. beam splitter some amount of variation is always possible.

There is nothing like a perfect material in this world ok detector also can introduce errors. So etc. all these things can introduce a little bit of phase errors in the final spectrum. So the phase corrections are also normally applied to reduce the photometric errors. So far I have talked to you about FT-IR ok. Next in your next class will start talking about sample handling, so what I had taught you today essentially is there are 3 types of instruments, filter photometers, grating photometers and FT-IR I have taught you the basic arrangement of the optical system. In these 2, 3 system and we will continue our discussion in the next class, thank you very much.