Optical Sensors

Prof. Sachin Kumar Srivastava
Department of Physics
Indian Institute of Technology, Roorkee

Lecture – 20

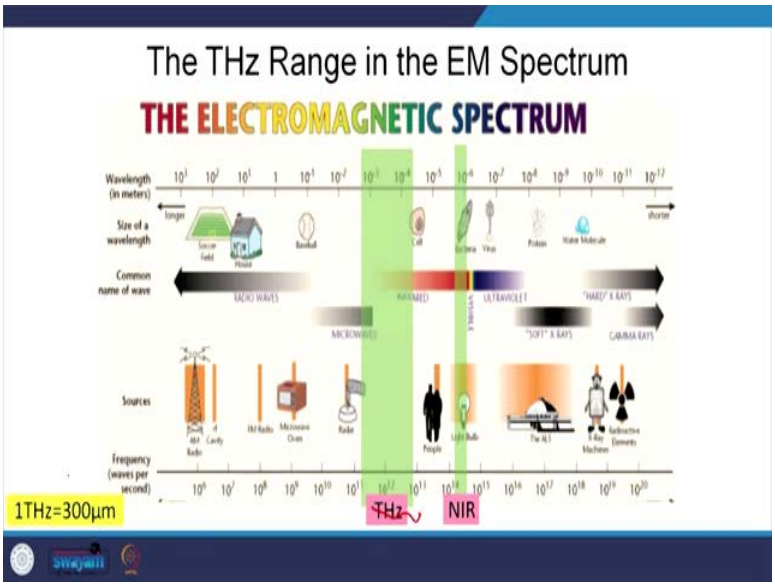
Terahertz Based Detection, Circular Dichroism Terahertz Applications, Chirality, Polarization Rotation and Dichroism

Welcome to lecture 20 and the final lecture of Optical Sensors course. Today we are going to discuss two different things: one is Terahertz waves and their applications in detection and the other part will be on Dichroism, in particular, circular dichroism and then how biomaterials respond to this kind of, well, you have polarization and all these things involved.

If you remember, in the last lecture, we discussed the optical response of various biomaterials - say for example, DNA, proteins, fat and we also discussed their various absorption windows. And we concluded that if they are absorbing in the spectral window, what you can do is that you can calculate absorption coefficients and absorption cross sections from there and then you can determine quantitatively and qualitatively the amount of that particular biomaterial.

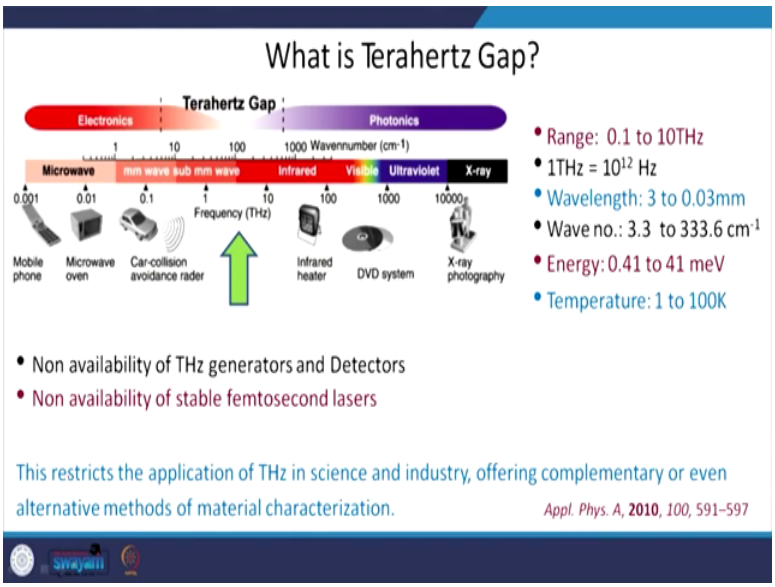
And we took couple of examples: one was hemoglobin and the second one was bilirubin, which was for jaundice prediction. Okay! Today we will go further, and we will pick up one very important and very hot topic of the day; that is terahertz. Now, everyone wants to do terahertz, but why? Why it is important we will see today and then how it can be useful for detection applications.

(Refer Slide Time: 02:14)



Tera means 10 to power 12, so, the frequency here is of the order of 10 to power 12 per second and if you say in meters it will be 10 to power minus 3 to 10 to power minus 4 and you can see that this lies somewhere in the middle of microwaves and infrared. Here is your NIR where you measured the bacteria and all those things, and when you come to terahertz, around roughly 300 microns in size, if you have entities below this wavelength, it would not see any difference. That is why you can use it for sensing of whole blood cells or something.

(Refer Slide Time: 02:48)



Terahertz gap: now there is a gap; I mean the field of electronics is full fledge developed and the photonics is developed full-fledged, but there is a gap at the juncture, where electronics and photonics meet. Actually, you do not have detectors or sources in this particular range, that is that is why it is called terahertz gap and there are no available femtosecond lasers also.

This range which is around 0.1 to 10 terahertz means 3 to about 0.03 millimeters of wavelength range, we do not have much terahertz generators and detectors. So, it is an open avenue for research and lots of, now, research is going on to make terahertz generators and terahertz sources. People have succeeded also to make laser like terahertz generators or polychromatic also.

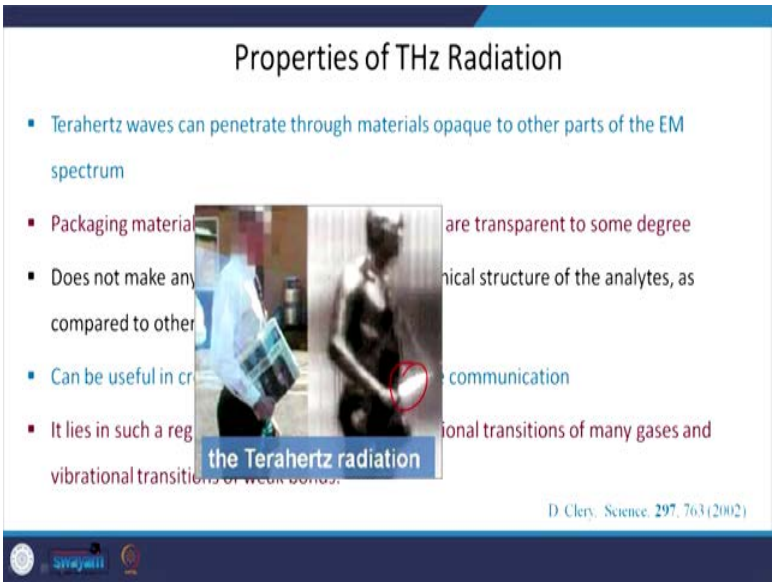
So, their applications we will see. What is important is that if you make this kind of thing - previously it was not available, so it restricted, you know, its use in exploring the science and industry, but nowadays it has become more and more relevant. So, why is it relevant? Because they can penetrate through the medium which are even opaque to say other parts of the electromagnetic spectrum; that is something very beautiful.

For example, if you have a plastic bag or wood (Refer Time: 04:23) or if you have a briefcase, it can become transparent to some extent to this kind of waves; that is the beauty of this. And since they have very small energy, not as much high energies like x rays or something, they do not make any substantial change in the chemical composition of the - chemical structure of the – analyte: it is also very important aspect. And you can create images as I told you that the briefcase is transparent to this kind of wave then you can see what is behind it yeah.

So, it can be used for creating images and take spectroscopic data and also it is nowadays have been sought to be used in short range communication. Why? In Wi-Fi or something because, now since it has relatively higher energy than the microwaves and radio waves, you want to use this range of spectrum to enhance the Wi-Fi signals - it will be enhanced communication. So, the data rates will be larger; better and more importantly you can study rotational spectra and vibrational transitions using this.

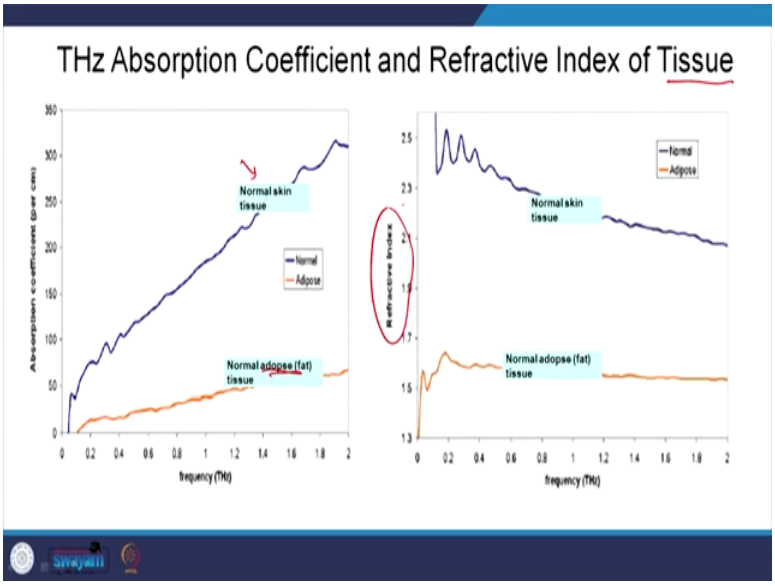
Because it is on the verge of far IR, you can still have, you know, combinational analysis of materials which lie between microwave and IR. So, that is the beauty of terahertz.

(Refer Slide Time: 06:06)



For example, you can see that this man - in a general image, is carrying a paper, but if you look using terahertz, what you see is that he is actually carrying a knife. I mean the paper is transparent to terahertz. So, you can see what is behind it. See how beautiful it is.

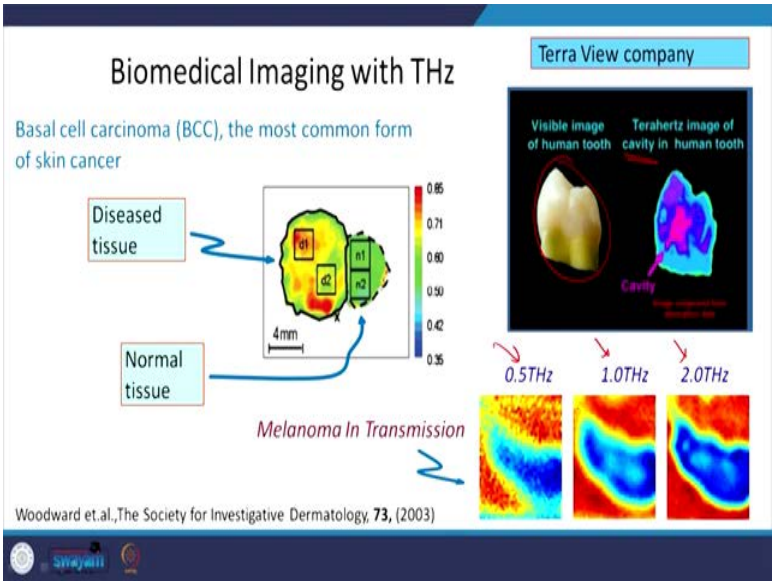
(Refer Slide Time: 06:24)



You will see a few applications. When it comes to tissues, for example, we have taken a couple of tissue, this is normal skin and this is a fat tissue and you see that their absorption coefficients in terahertz region are different. So, even if they look the same,

they have different absorption, because they have different refractive indices in this region. So, it is very easy to see how it changes in terahertz.

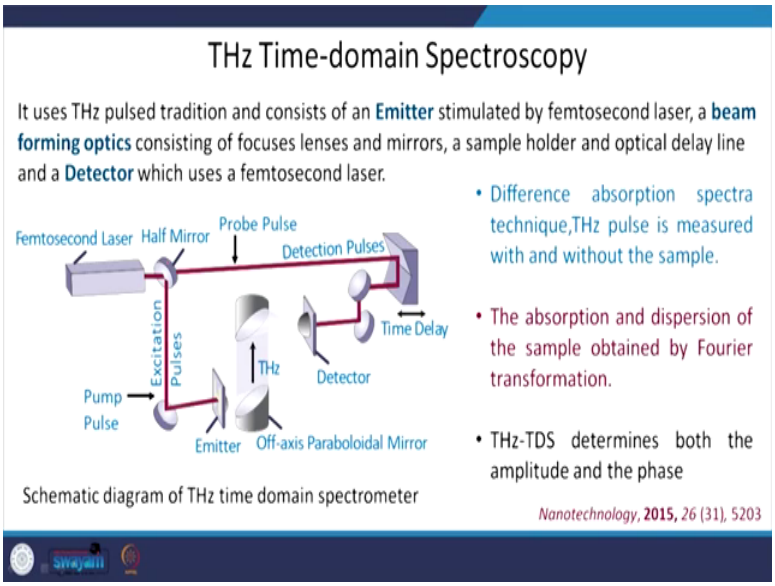
(Refer Slide Time: 06:51)



You can use it for biomedical imaging, for example, if you have a cell - a part of it has some disease and then you can see that in the imaging that diseased tissue has shown these areas which are highlighted in color and normal tissue does not have this disease so it is like that. Here is another example from Terra View company, where they did an imaging of a tooth.

In visible light, you see that it is a fine tooth, but when you see with terahertz you find that – no - there is a cavity in the human tooth, and you can determine - by changing the wavelength of it, you can assess various contrast images and then you can know that what is the size of the cavity and what is the depth also. So, these are kind of examples which show that how useful it is. We will come to more examples.

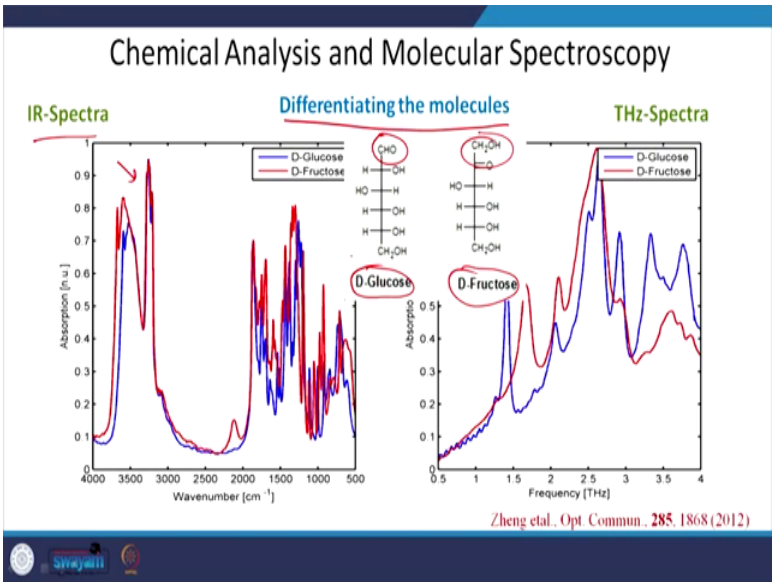
(Refer Slide Time: 07:48)



But, let us see what terahertz time domain spectroscopy is. This is spectroscopy which measures actually the absorption spectra with and without the sample from the terahertz pulse. So, what you do is that you measure the absorption and dispersion of the sample by using Fourier transform. It gives you both, I mean, amplitude as well as the phase.

So, what is there actually? You have a femtosecond laser which excites pulses and then you have an emitter which emits from this femtosecond laser; you get the terahertz source. So, it becomes a terahertz source and then you have it pass through the sample and you have another pulse from the femtosecond laser, which is actually a probe source. It takes care of how much change in phase occurred, ok! That is how you use it for time domain spectrometry.

(Refer Slide Time: 08:45)

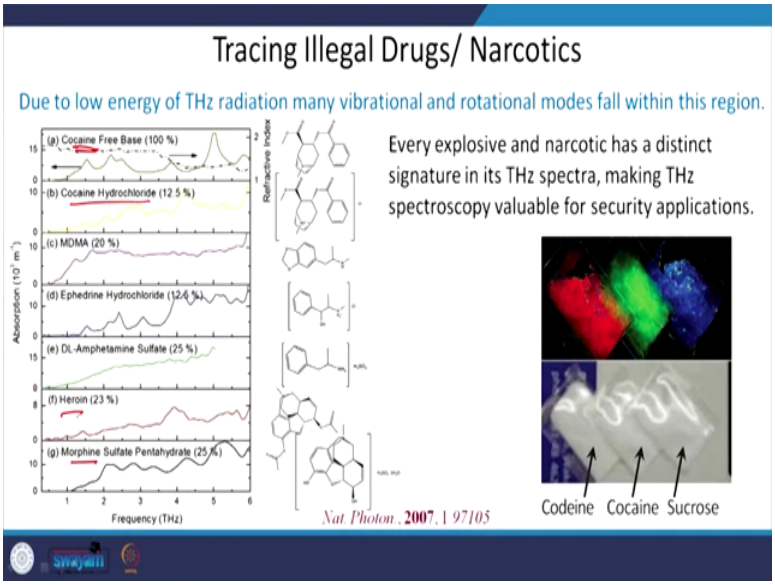


There are various applications of terahertz. One of them is differentiating the molecules. Suppose I have 2 molecules, which are almost similar in chemical composition, say we have chosen glucose and fructose. They are almost same in chemical composition. There is only one difference that - it has an aldehyde group and it has a ketone group, that is it! So, most of the bonds are basically similar like CH bond, COH bond, and that is why you see that in IR spectrum - you do not see much difference; they are all same - almost same for glucose and fructose; while in terahertz, you see that they both have distinct absorption curves. That is the beauty. I mean, you can differentiate between 2 molecules, which are even similar in IR spectroscopy; and in terahertz, you can see that they are distinguishable. You can use it for tracing of illegal drugs or narcotics, why? Because this has many vibrational and rotational modes which fall in this region. So, it can be used to, you know, excite those rotational and vibrational modes and then you can say this is at this particular compound, I mean, it is like - similar to IR or rotational spectroscopy.

For example, here you can see that this is a base cocaine and cocaine hydrochloride and MDMA - different kinds of - heroin and morphine. These have different absorption curves in terahertz and that means, that if you have a matrix of elements from there you can say that – ok - we have cocaine or cocaine hydrochloride or morphine or heroin and also based on the absorbance you can say that how much.

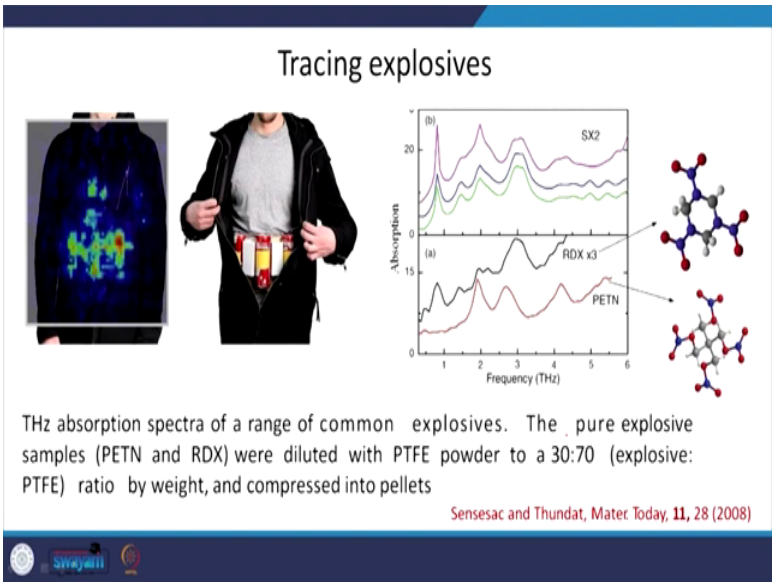
So, it can tell you qualitatively and quantitatively both. Because it has distinct signature in terahertz as you can see that all of them have different, distinct signatures, you can directly relate it to what kind of material it is and then even you do not need open the box. If you remember that I told you that terahertz can penetrate though certain plastic material.

(Refer Slide Time: 11:16)



So, if you have a box full of narcotics or illegal drugs, you can immediately tell that what kind of drug is in the box without even opening it. You see there are different materials. They have different spectral signatures.

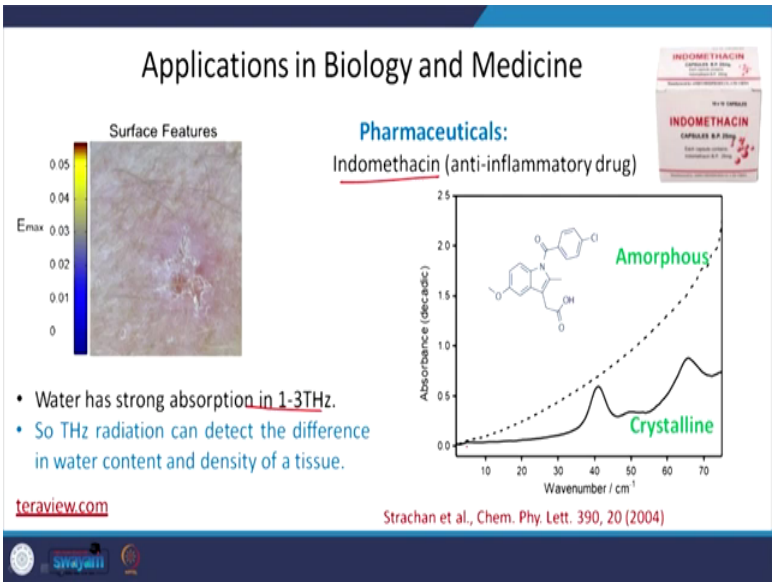
(Refer Slide Time: 11:29)



It can be used for tracing explosives. Here you see that if you are hiding an explosive, you hardly can see from outside, but by using terahertz you can say if we illuminate the body with terahertz you can say ok, now I am getting some signals which means you have something here. And then you open it - the zip and you find there are explosives.

You can see the absorption spectra of SX 2 and RDX here and PETN and you see that they are different. Again, it is not just narcotics, but explosives also have distinct absorption spectra in terahertz region. Without using any sophisticated mechanism for making a sensor, what you can immediately do is that you shine on terahertz light and detect the spectra and or can do an imaging and using both you can say that ok you have this particular explosive even from a range, you do not need to be near the person.

(Refer Slide Time: 12:38)



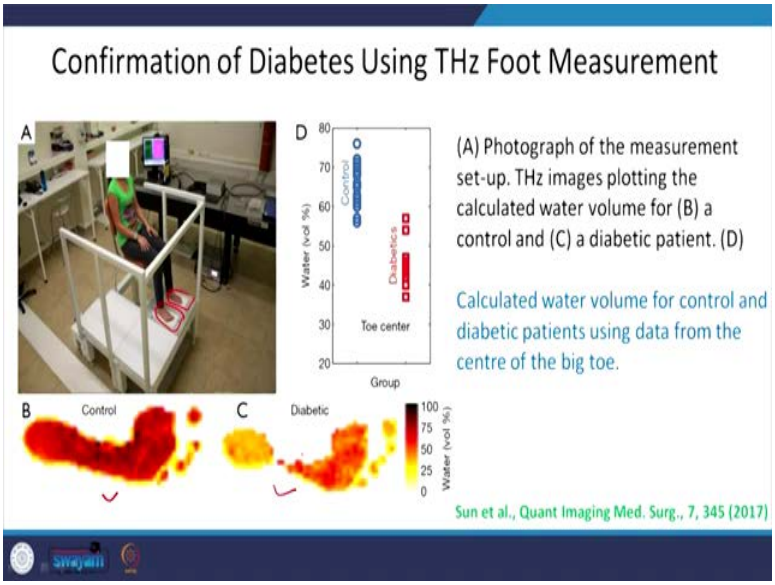
It is used in biology also and medicine. Here are a couple of examples. Because water has strong absorption in 1 to 3 terahertz, that means that terahertz radiation can detect the difference in water content. Suppose you have couple of tissues and one of it has larger water content than the other, then if you do a surface profiling, then you know, you can convert it into an image and that will give you the surface features of that particular surface.

If on my hand if I have inflammation or something, probably the water content will be different from the normal tissue and that you can detect easily using imaging from terahertz. There is another example of detecting pharmaceuticals. In pharmaceutical industry, you have, say one example is Indomethacin, which in an anti-inflammatory drug and you see that the amorphous and crystalline structures of it have different absorbance in terahertz region. So, suppose you want to make a tablet of this particular drug and then you come -OK – no, it is not crystalline; it is a amorphous one and I do not want amorphous one.

So, it is not just that you determine the chemical composition, but also the crystallinity, which makes an impact here when you measure the absorbance spectra in terahertz region, that is something very important! Because the same compound has different absorption spectra and that determines, I mean, sometimes you do not want amorphous

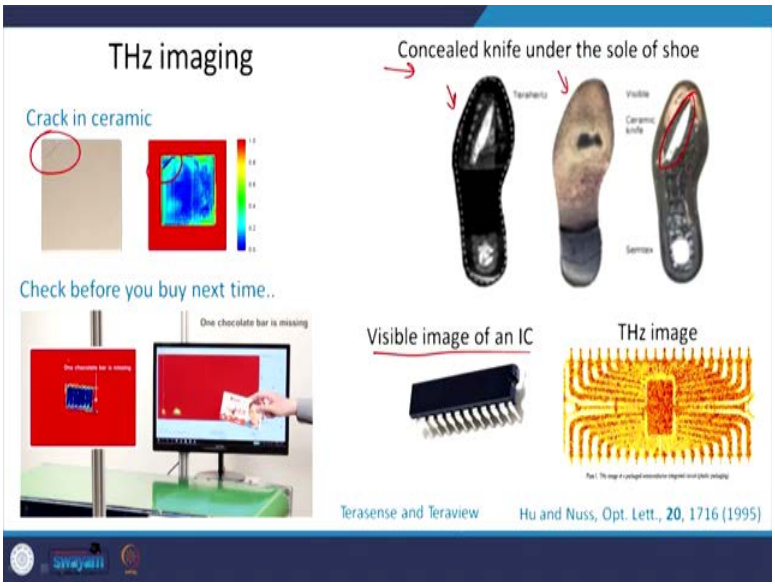
ones or crystalline ones or vice versa. So, that helps us choose what kind of phase also of the same material is required for making a pharmaceutical.

(Refer Slide Time: 14:32)



Confirmation of diabetes using terahertz foot measurement: what it means? It means like you can see here that a lady is sitting here and beneath her foot there are sensors for terahertz imaging and then they are photographed and you can see that based on the water content level, this is normal one; this is a diabetic one and you can see easily that how much is the difference. And based on this imaging technique, not only you can say that a person is diabetic or not, but you can also say that how much is the blood glucose concentration. So, it is both qualitative as well as quantitative.

(Refer Slide Time: 15:24)



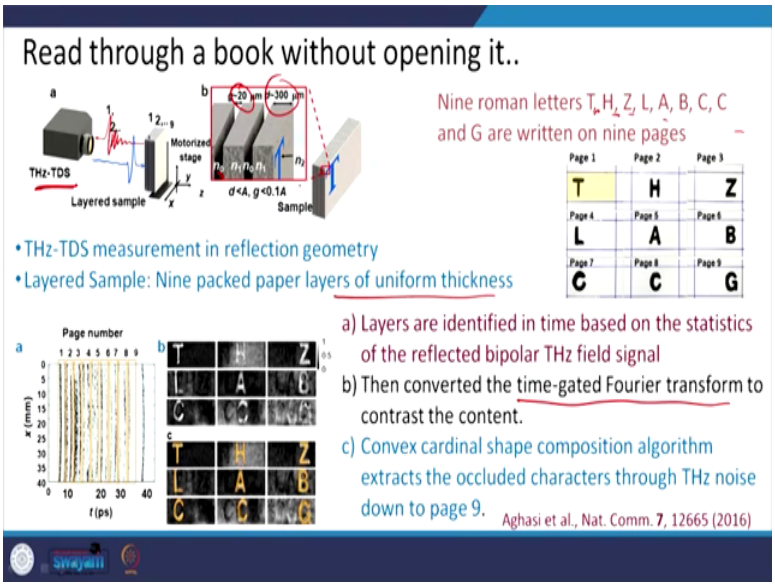
It also can be used for imaging. If you have a minute crack in a ceramic, you can do an imaging and you can see the crack - you can see here which was here, sometimes it can detect even minor cracks. I mean, when I am talking about it, it is a few microns crack. I am talking about those which are not visible through eye. You can also see concealed knife under the sole of a shoe. This is the normal picture of the shoe sole and this is the picture taken using terahertz and – ok - then you say no; you have knife and then you take off the sole and then you find the knife is here.

This can be used in defense; you know, at security checks, it is something very important. This is visible image of an integrated chip and you can see that if you do in terahertz you can see all the connections and if they are connected - well connected or not. Sometimes when you do a manufacture, you can see that you do not see any connection here, sometimes this leg is not working. So, you know that using terahertz for quality test that this chip is good or not.

Here is another example. This is a chocolate box. When imaged with terahertz, you see that one of the chocolate bars is seen missing. So, if you go to a supermarket, suppose you have a terahertz scanner, then you will know that ok - whatever I am buying and in a packaged food or packaged any item- if it has the same quantity or quality or not.

So, these are some of the uses where we can use terahertz and use the spectroscopy technique.

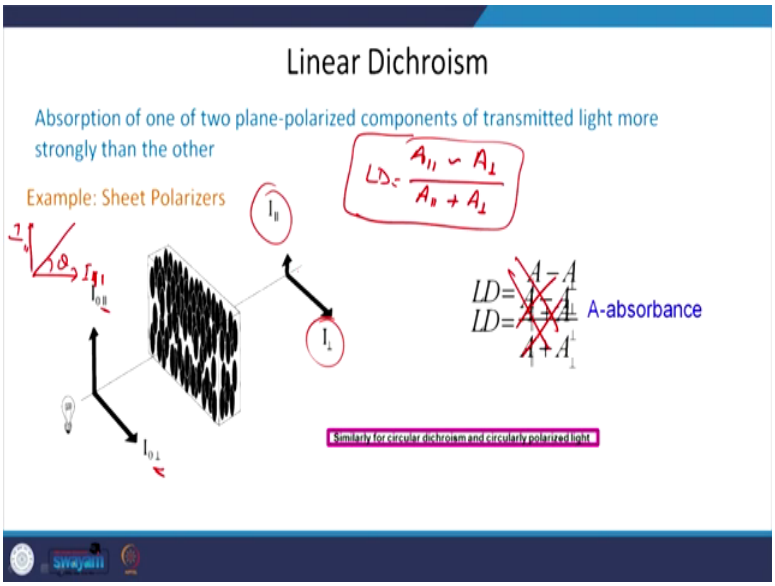
(Refer Slide Time: 17:10)



Here is a use of terahertz TDS which we already discussed and using this technique you can read through a book without opening it. Here what they did is that they took 9 pages and each page was of uniform thickness and then they wrote this letter T H Z… something like these (Refer Time: 17:36) on 9 pages. And they made a stack with every paper with a gap of 20 micron and the thickness of each paper was 300 micron and on the backs of it was written. And the reflective indices of the gap is n 0 and that of the paper is n 1 and n 0 and n 1 so forth.

Using a motorized state and using TDS, you can say that you can image each page and what you do is that you take a time gated Fourier transform to access this information from terahertz signal that, what is there on the back of each of the pages, even without opening the stack.

(Refer Slide Time: 18:23)

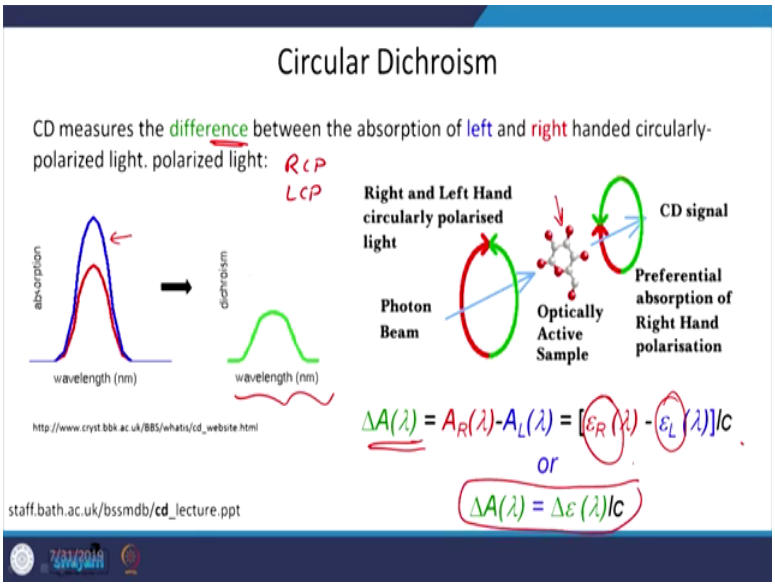


Let us see what dichroism is. This was all about terahertz till now that we studied that what is terahertz and what are the miracles it can do. Something is wrong here; I will write it correctly.

If you have a material and you shine with 2 orthogonal polarizations say what I am shining is I parallel and I perpendicular. What happens actually that out of these two polarizations absorbs one of the polarizations stronger than the other. So, what will happen is that it will lead to change in the polarization direction, because now the polarization components have changed. So, suppose you had polarizations like this at an angle theta and suppose you can have I parallel and I perpendicular, which are given by I cos theta and I sine theta.

And now what you see is that this I cos theta and I sine theta have changed because now the intensities of parallel and perpendicular components have changed. So, what you get is that the absorbances are different and that is called dichroism. When it is for linear polarization, it is called linear dichroism. So, that is defined by absorption parallel difference absorption perpendicular divided by absorption parallel plus absorption perpendicular - that is the linear dichroism. Forget about this, ok.

(Refer Slide Time: 20:15)



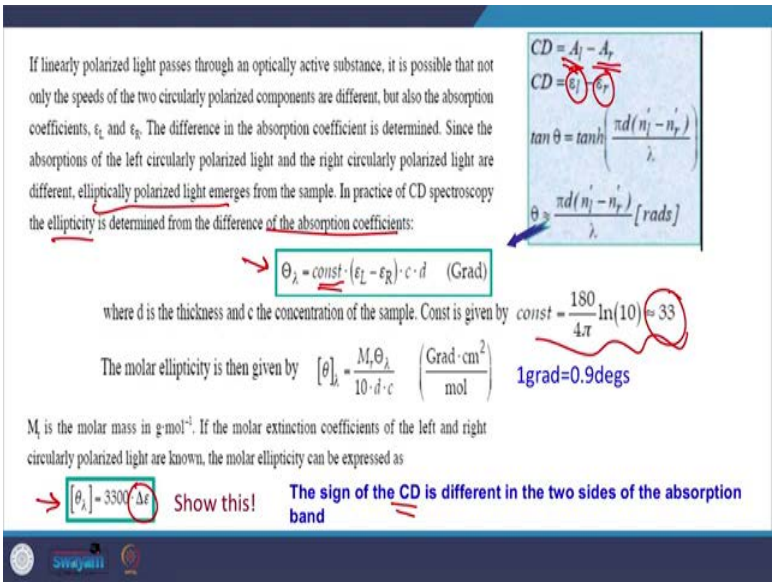
When it comes to circular polarizations, it is basically the difference between the absorption of left- and right-handed circular polarized lights. So, you have RCP - you have LCP and they are different.

Suppose one of them, say, the blue one is left circular polarization; red one is for right circular polarization, then what you get is the difference of these two that is the green one - this gives the dichroism. From the absorption spectra for 2 orthogonal polarizations, you can say you can extract the information about the dichroism property of materials. If you have circular polarizations, then it is circular dichroism. So, it is depicted here.

Suppose you have a beam which has green one and red ones showing two different polarizations: say right and left circular polarizations, and they are equal in magnitude and once it is incident on an optically active sample, what happens actually? That is the green; the red one has absorbed more; that means the right one, and the left circular polarization is not absorbed more. So, it is showing a large component here.

So, this is the difference between the absorption and that can be converted in terms of the absorption coefficient for right and left circular polarized light divided by the concentrations. So, you get this relation - this gives the circular dichroism of this material.

(Refer Slide Time: 21:58)



Let us emphasize on it more. So, CD was like difference between the left and right circular polarized absorptions. Actually, it is not absorption, but it can also be difference between the absorption coefficients.

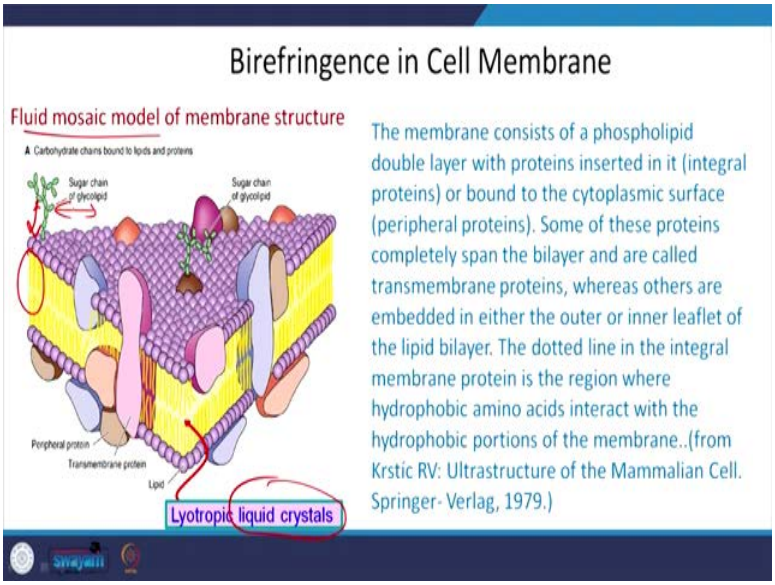
So, what happens actually? That now you have linear polarization you can convert it into 2 orthogonal circular polarization that is left circular polarized and right circular polarized. It passes through the material and then it superimposes again what will happen? You will get an elliptically polarized light. You shone on it a linear polarized light at 45 degrees. So, it has like both right and left circular polarized lights and then you get elliptical polarization from it.

So, in practice, in CD spectroscopy, ellipticity is measured by the difference in absorption coefficients given by this relation, where this constant here is given is around 33 and if you solve for it using molar ellipticity and all these values the sign in CD is this. This is basically delta epsilon which is the difference in the absorption coefficients.

Birefringence: why it comes actually? Why we will get circular dichroism or dichroism? Because you have birefringence. Birefringence - we say now the molecules are anisotropic, and they are responding differently for different polarizations. One of the examples is, I mean, since we are considering here bio-materials, it is collagen fibers.

You have some orientation order that will give you form birefringence and this form birefringence has a polarization dependence. So, you can create form birefringence.

(Refer Slide Time: 24:04)

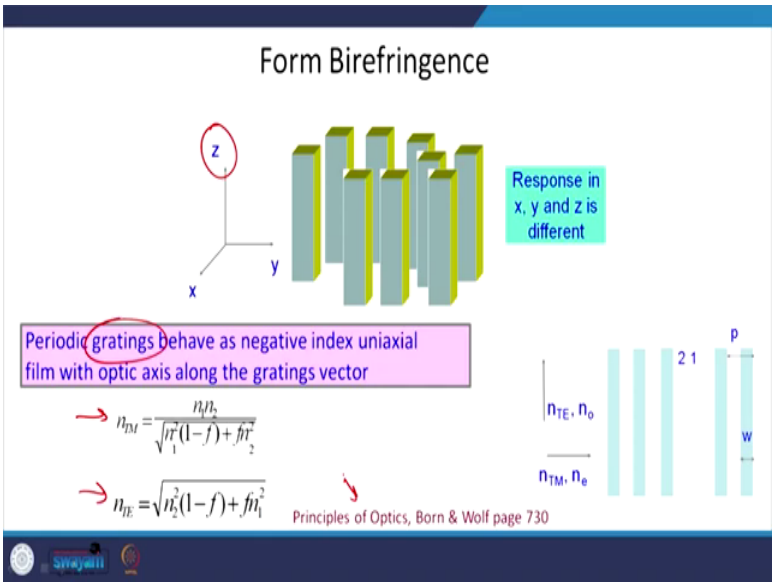


In a cell membrane you see that it has - I am showing a mosaic model, where you can see that it is made of something similar to lyotropic liquid crystals. This consists of these double layers of proteins and all we have to think about it is this organization of these protein layers which are like liquid crystals. They are round shaped. They will behave- for light falling of this polarization - differently than this polarization.

You can have birefringence in cell membranes also. It is very important if you are going even to study the skin or any other bio-material you have to consider the polarization dependence also.

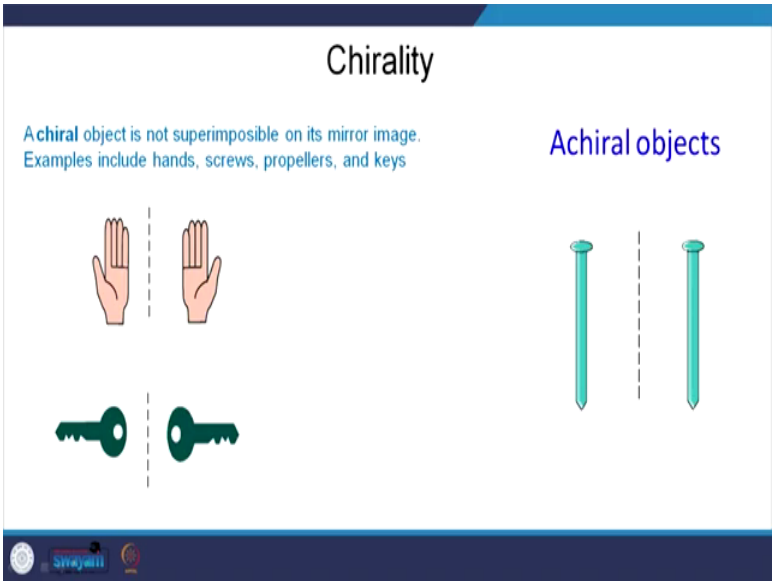
So, it is very important that you know CD. All you care about is that you send 2 orthogonal polarizations and at the end of it, in the reflection or in transmission, you see that how much change occurred and from there you can conclude about the structure or the dichroism involved in the structure.

(Refer Slide Time: 25:19)



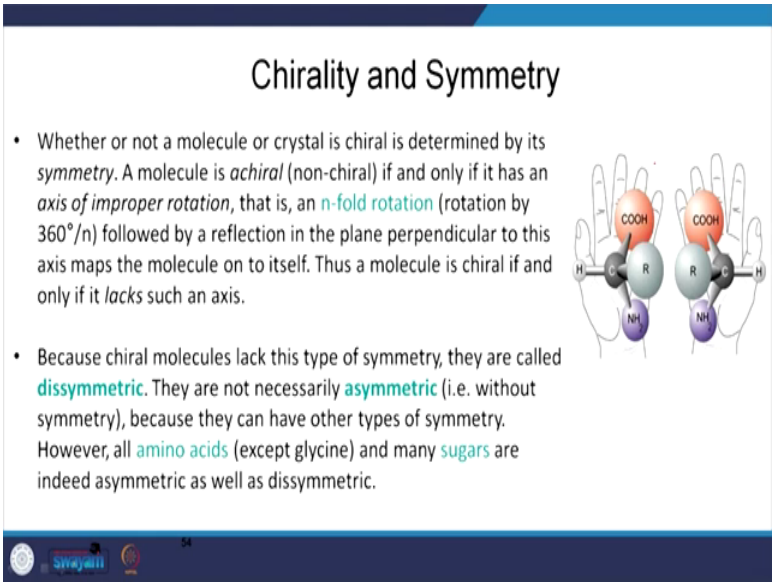
Form Birefringence - you can have periodic structures which basically form to have different refractive indices along different polarizations. So, if you have its elongation in the z direction what you see is that T is given along z and TM is perpendicular to this stack. So, they will have different refractive indices which are given by this relation and if you want to learn more about this - f is the filling factor here - it can be consulted from Born and Wolf, page 730.

(Refer Slide Time: 26:04)



Chirality: An object is called chiral when it cannot be superimposed on its mirror image, For example, this hand. If you put this hand, its mirror image is this. If you put like this, it does not superimpose. You have this, its mirror image will be its opposite - like this; if you put on there, it will not superimpose. These kinds of objects are called chiral. This kind of objects are called achiral - like the mirror image can be superimposed on it. So, in English if you want to see the letters like T, I, O - these are all achiral; r is chiral, c is chiral, e is chiral - like this.

(Refer Slide Time: 27:14)



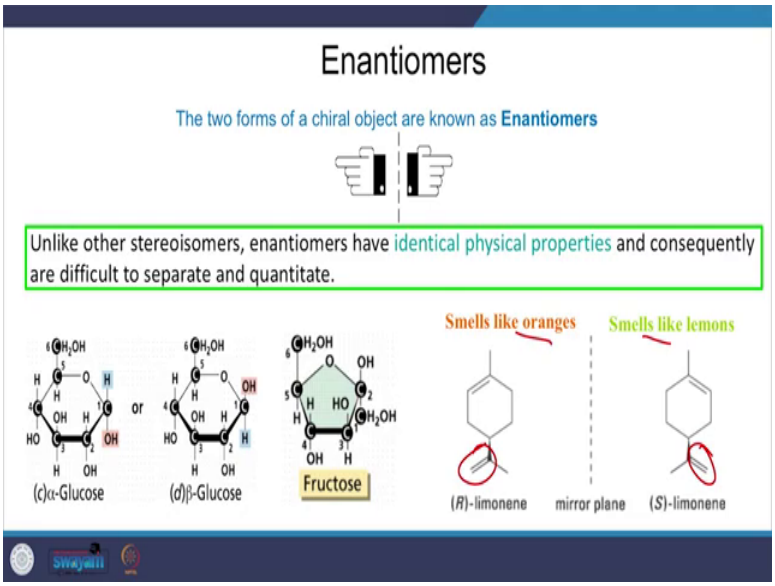
There is a relation between chirality and symmetry. If the molecule is asymmetric or say dissymmetric, then they are chiral. For example, this molecule you can see that they do not superimpose on each other. So, what it means is that - if you have symmetry then the molecule is achiral, and it is determined by the rotation - axis of improper rotation. If it is followed by the reflection and plane perpendicular to this axis match the molecule onto itself, this molecule is achiral; if it does not do that, then it is chiral.

Enantiomers: What are Enantiomers? These two forms of chiral objects which are not able to superimpose are called enantiomers together.

Enantiomers have identical physical properties because they are the same - this end is similar to this hand; it also consists of 5 fingers this also is a palm, this is a palm it is the same.

So, it is very difficult to, you know, make a qualitative analysis or quantitative analysis most of the times. I gave you an example of glucose and fructose. You can see that they have similar composition group, if you write the formula for - chemical formula for glucose and fructose, they are same. So, they are enantiomers actually. If you superimpose them you do not get -for example, this alpha glucose and beta glucose if you put them together they do not superimpose.

(Refer Slide Time: 29:02)

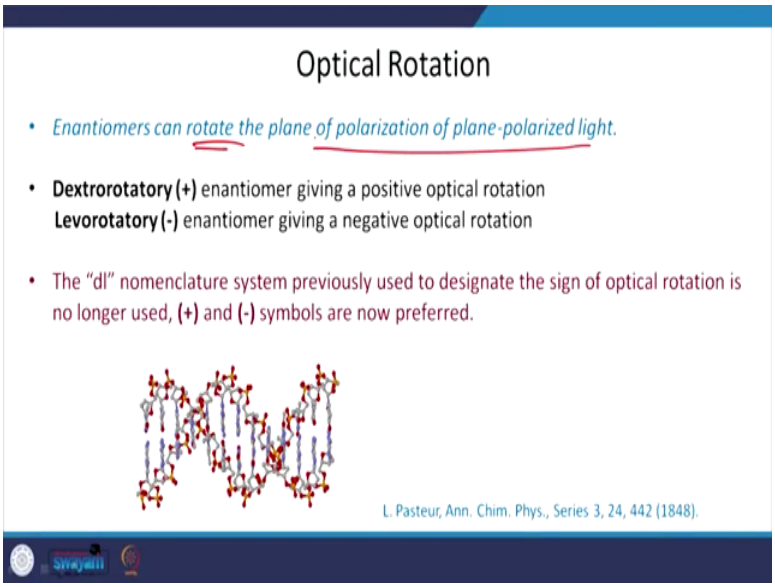


Another example is limonene: (R)-limonene, (S)-limonene. You know, you see these bonds here that is the difference and it smells like lemon; it smells like oranges, so these are different. It gives you optical rotation because it can rotate the plane of polarization of plane polarized light. So, let us connect it all.

We were talking about circular dichroism that was all about having different absorptions. Because of different absorptions of different polarizations in dichroism, hat you have is - the rotation of the plane of polarization. That is because of chiral molecules and these set of chiral molecules can be called enantiomers and they can rotate the plane of polarization of the light. They are called dextrorotatory or denoted by plus sign if enantiomer is giving positive rotation. So, if it was at angle theta one now it is going to theta 2 and theta one is smaller than theta 2, it is called dextrorotatory.

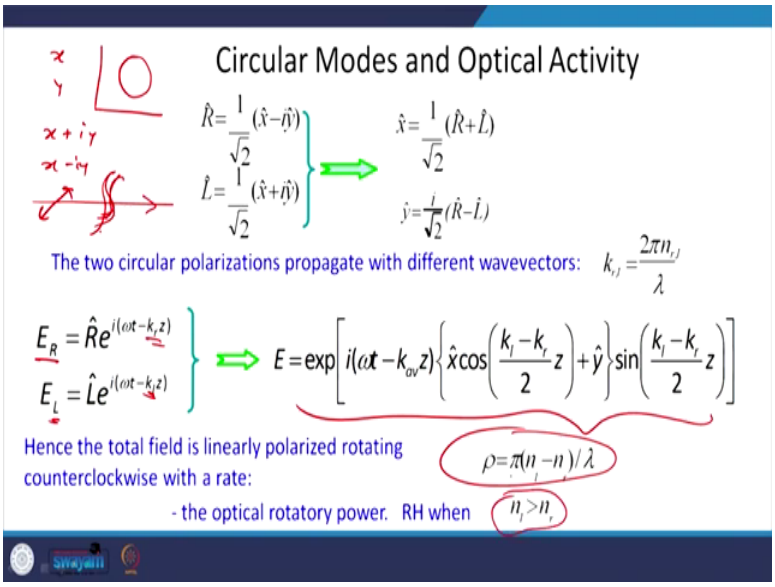
If theta 2 is smaller than theta 1, then it is called levorotatory. Before that was called d rotatory or l rotatory, but now this designation (Refer Time: 30:31) now is not used in nomenclature now it is what this thing is.

(Refer Slide Time: 30:37)



Suppose you have this kind of a DNA. It is a chiral molecule. So, it can rotate different polarizations in different angles and based on that, you can calculate the circular dichroism for this.

(Refer Slide Time: 30:55)



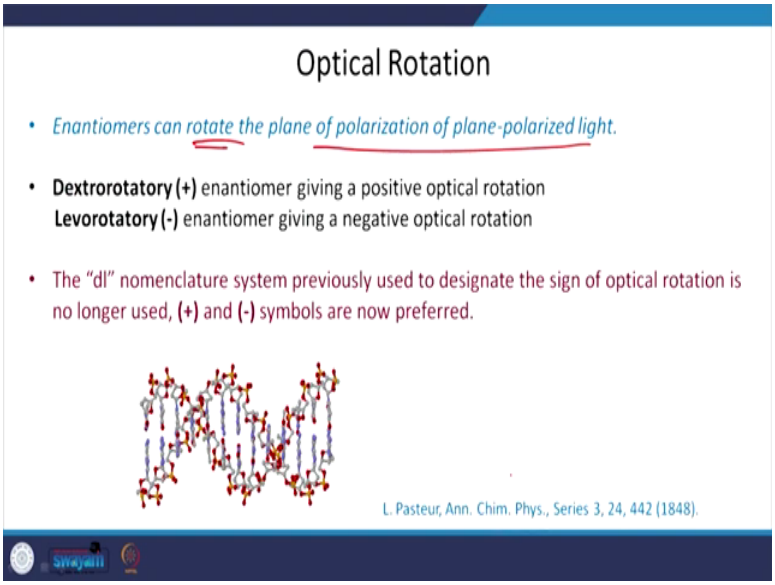
What happens actually that you have x and y polarizations on axis. What you can do is that you can have a circular polarized light. You can always - it will be x plus y i y or x minus i y- write it like this. Right circular polarization - this can be broken into 2 parts that are linearly polarized. If you remember, when we are discussing polarization, I told you that any polarization can be resolved in a set of 2 orthogonal polarizations.

So, if you have x and y linear polarization, so a circular polarization can be converted into linear polarizations x and y. Similarly, a linear polarization can be termed in terms of 2 orthogonal circular polarizations. A linear polarization can be a combination of right circularly polarized light and left circular polarized light - that is what I have written here.

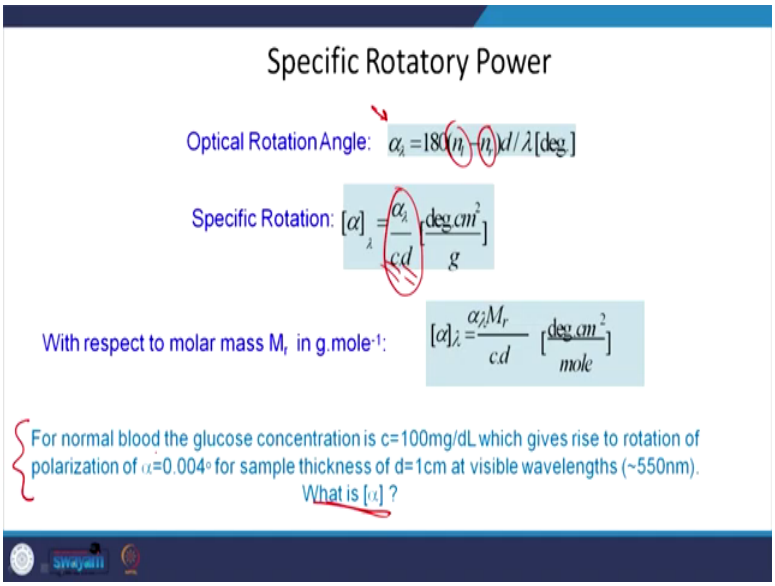
So, you have certain linear polarization it passes through the material, suppose DNA here and then what you get here. You have 2 circular polarizers orthogonal to each other and then you are trying to see that what are the absorption coefficients for these 2 circular polarizations.

These 2 circular polarizations propagate with different wave vectors. E R will have a wave vector k R, E L will have vector k L. So, total superimposed one will have this wave vector. So, total field is linearly polarized rotating counterclockwise with a rate this and optical rotatory power is right-handed, when this is positive; it can be negative also as we discussed during circular dichroism - we will see.

(Refer Slide Time: 33:01)

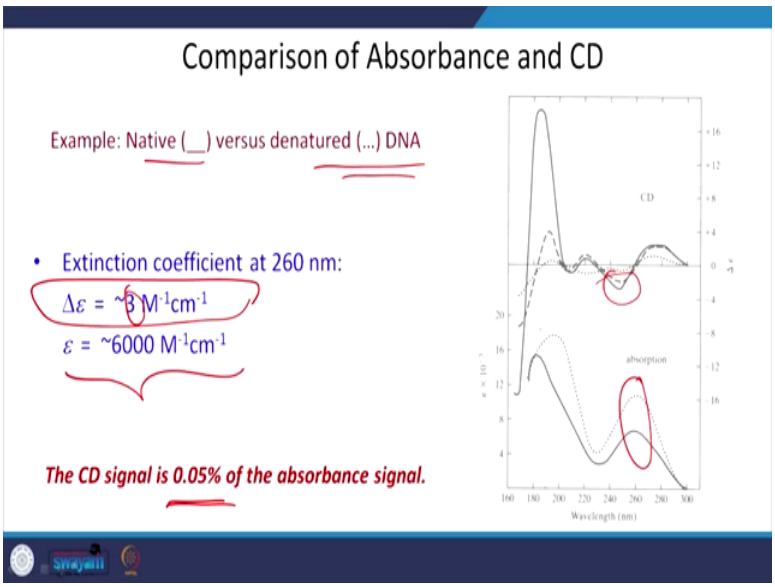


(Refer Slide Time: 33:02)



Optical rotation angle is given by this relation, which is dependent on n l and n r, which are for the left circular polarization and right circular polarized lights. And the specific rotation is given by this relation, where you have concentration and d is the thickness of the cell(Refer Time: 33:19), because if you have a larger thickness then the specific rotation will be larger and then with respect to molar mass, you can have this relation. I am giving you a homework that you go and calculate alpha for normal blood glucose concentration, ok!

(Refer Slide Time: 33:39)

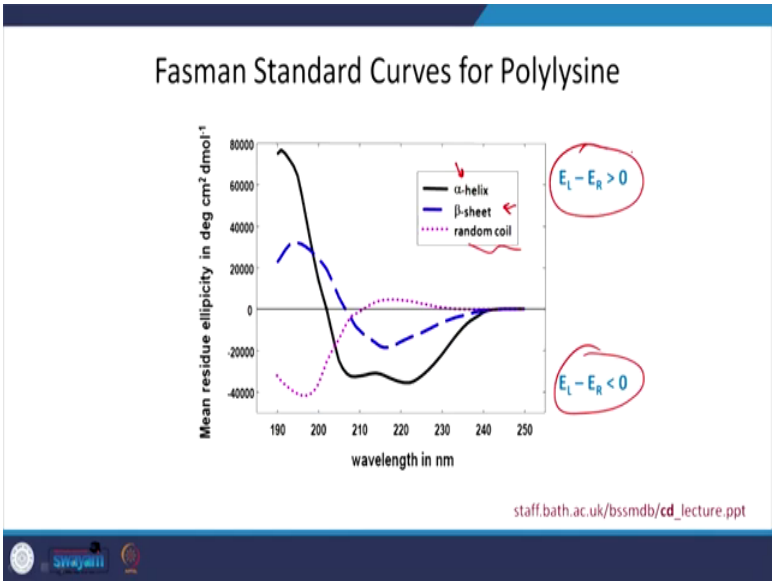


Now, we know that if we have a molecule, it can have circular dichroism and it can rotate the axis of the linearly polarized light, which was incident on it. Because the left circular polarized light and right circular polarized light - they have different wave vectors, their propagation constants are different and they can also move in different directions, ok.

What are the implications in the real samples? Here I have shown you the native and denatured DNA - the CD spectra and absorbance spectra here. You see that absorbance spectra are similar, but you see the difference in absorbance, but these bands are same, and here also you see that it can go negative also - this in CD.

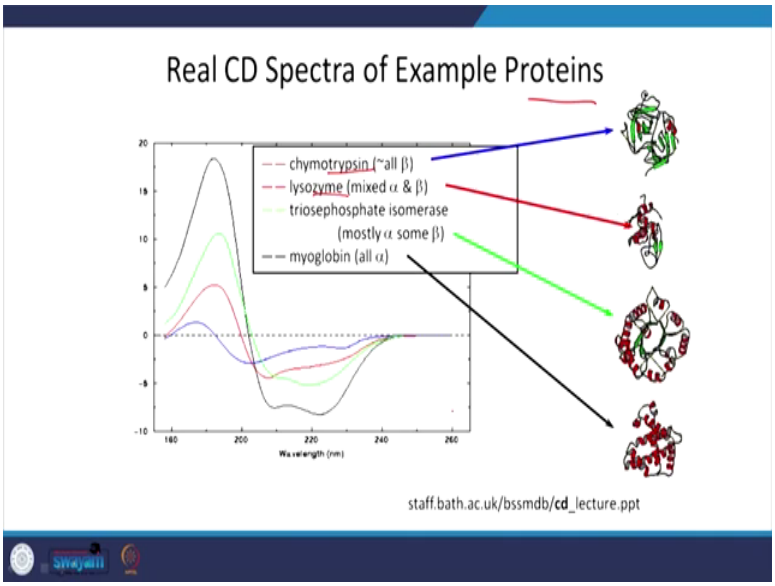
The extension coefficient at, say, this wavelength around 260 nm, this is of the order of 6000 mol universe centimeter inverse, but when it comes to difference between absorbance coefficient for left and right circularly polarized lights, it is only 3 - only 0.05 percent of the absorbance signal. So, it is very weak phenomenon; it is not so easy to detect. You have to have very highly sensitive spectrometers and power detectors.

(Refer Slide Time: 35:03)



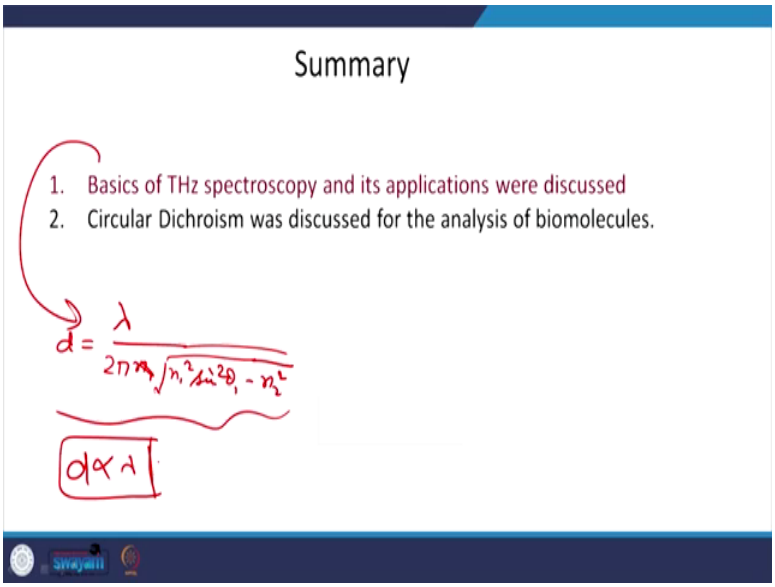
There are standard curves, we have plotted for alpha helix, beta sheet and random coil and you see that it can if this is less than 0, you have negative one; this greater than 0, you can have positive value of circular dichroism. So, from there you can conclude that what is the value of circular dichroism with respect to this particular polarization.

(Refer Slide Time: 35:30)



I am showing you now real circular dichroism spectra of proteins. This is chymotrypsin, lysozyme, triosephosphate, isomerase and myoglobin and you see that in different regions, they have different circular dichroism here, ok!

(Refer Slide Time: 36:01)



Let us conclude this talk. Today we discussed the basics of terahertz spectroscopy and its applications in large and we saw that how useful it is because of that inherent range of electromagnetic spectrum we have in terahertz - that it can probe the rotational as well as

vibrational spectra of certain molecules, which cannot be done by other methods - in other range of electromagnetic radiation.

That is how, it becomes very useful. And also, for certain materials, it can penetrate through it, so you can have noninvasive detection. And secondly, we discussed circular dichroism and also showed that what leads to change in the rotation and what are the factors on which it depends and how to measure it.

Something very important here I want to tell about this terahertz spectroscopy is that - if you remember that when we were discussing the evanescent wave sensors or surface plasmons, we had this penetration depth, which was lambda upon 2 pi n 1 square root n 1 square sin square theta 1 minus n 2 square. You see that this d was proportional to lambda. We know that now we are working in terahertz, so we have larger lambda. If you are working on an evanescent wave sensor in terahertz region, what you can do is that you can probe to large distances using evanescent field.

Then you can have an imaging or spectroscopy using evanescent waves (Refer Time: 38:01), its penetration - will be about of the orders of few 100s of microns or maybe a millimeter or so, because of the wavelength - which is almost the same range of the wavelength. So, it is about 300 micron or more. So, that is how you can even penetrate through and have a noninvasive sensing using terahertz.

Thank you.