Structure, Stereochemistry and Reactivity of Organic Compounds and Intermediates: A Problem-solving Approach
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Lecture 14
Introduction to linear Polarized light and Interaction with Chiral Materials

Welcome back to this course on Structures Stereochemistry and Reactivity of Organic Molecules and Intermediates, a problem-solving approach.

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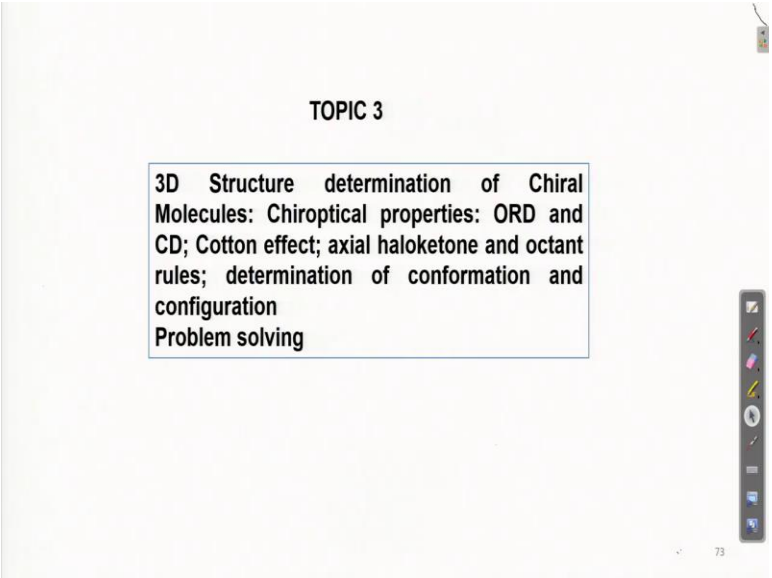

TOPIC 3

3D Structure determination of Chiral Molecules: Chiroptical properties: ORD and CD; Cotton effect; axial haloketone and octant rules; determination of conformation and configuration
Problem solving

Now today will start a new topic which is the topic 3 of this lecture series. Remember topic 1 and 2 are basically dealt with the stereochemistry of the various stereo chemical nomenclature systems, the symmetry elements, the point groups, the conformational analysis of bicyclic and try cyclic cyclohexanes absolute configuration assignment of actual helical and planar chirality those type of sterochemical issues we had discussed.

Now, the topic 3 is basically comes to that whatever we have written earlier, the question is how do people determine the structure of any molecule, especially of a chiral molecule because chirality gives an opportunity and extra opportunity to get some information based of the chiral nature of the molecule. So basically, this topic is structure determination of chiral molecules chiro optical properties I will explain what is this chiro optical properties.

And ORD and CD the full name is Optical Rotatory Dispersion and Circular Dichroism, cotton effect, axial haloketone rule, octant rules and determination of or basically application of these rules and the sign of the cotton effect in determination of the confirmation and configuration of molecules and will do some problem solving by the way. Now, let us start from the very beginning, very beginning of stereochemistry where it was shown that some molecules are there which can rotate the plane of plane polarized light. Either in the right-hand direction in the clockwise direction or anticlockwise direction.

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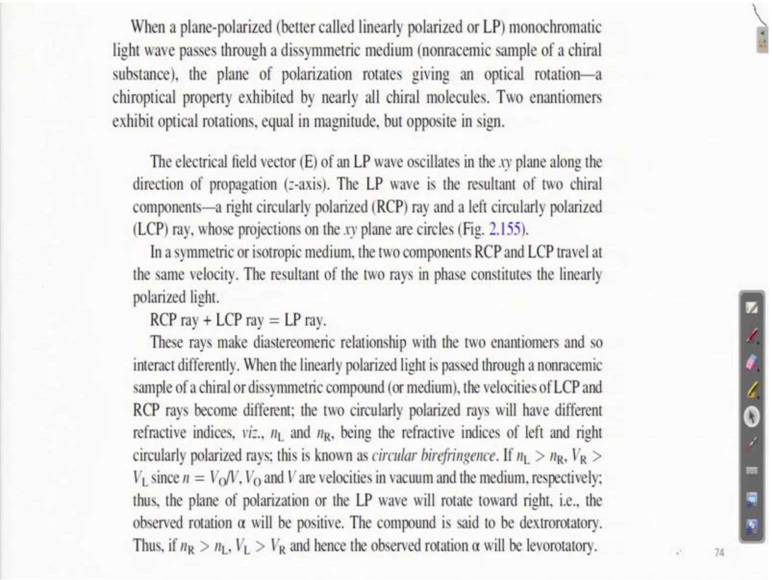


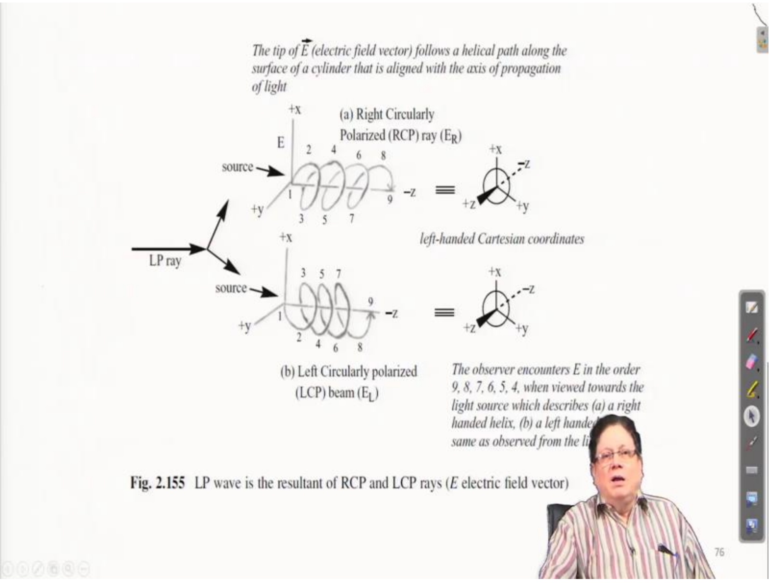
When a plane-polarized (better called linearly polarized or LP) monochromatic light wave passes through a dissymmetric medium (nonracemic sample of a chiral substance), the plane of polarization rotates giving an optical rotation—a chiroptical property exhibited by nearly all chiral molecules. Two enantiomers exhibit optical rotations, equal in magnitude, but opposite in sign.

The electrical field vector (E) of an LP wave oscillates in the *xy* plane along the direction of propagation (*z*-axis). The LP wave is the resultant of two chiral components—a right circularly polarized (RCP) ray and a left circularly polarized (LCP) ray, whose projections on the *xy* plane are circles (Fig. 2.155).

In a symmetric or isotropic medium, the two components RCP and LCP travel at the same velocity. The resultant of the two rays in phase constitutes the linearly polarized light.

RCP ray + LCP ray = LP ray.

These rays make diastereomeric relationship with the two enantiomers and so interact differently. When the linearly polarized light is passed through a nonracemic sample of a chiral or dissymmetric compound (or medium), the velocities of LCP and RCP rays become different; the two circularly polarized rays will have different refractive indices, *viz*., n_L and n_R, being the refractive indices of left and right circularly polarized rays; this is known as *circular birefringence*. If $n_L > n_R$, $V_R > V_L$ since $n = V_O/V$, V_O and V are velocities in vacuum and the medium, respectively; thus, the plane of polarization or the LP wave will rotate toward right, i.e., the observed rotation α will be positive. The compound is said to be dextrorotatory. Thus, if $n_R > n_L$, $V_L > V_R$ and hence the observed rotation α will be levorotatory.



The tip of $\vec{E}$ (electric field vector) follows a helical path along the surface of a cylinder that is aligned with the axis of propagation of light

left-handed Cartesian coordinates

The observer encounters E in the order 9, 8, 7, 6, 5, 4, when viewed towards the light source which describes (a) a right handed helix, (b) a left hande same as observed from the li

Fig. 2.155 LP wave is the resultant of RCP and LCP rays (*E* electric field vector)

So question is, if you go to the little bit deeper that what is the, what is meant by a plane polarized light, I think that is also known to you that plane polarized light is basically at the light where the, sorry the light where the vibrations like the electron same electrolyte is electromagnetic waves, so you have to (())(3:23) as electric component and the magnetic components. So, in electric vector and magnetic vector which are making at right angles to each other.

So if we consider the electric vector, the electric vector, what happens the electric vector vibrates in a plane in a particular plane and not a all the different planes that are possible when light travels and the traverse part you can have several perpendicular arrangements or perpendicular planes possible but ordinary lights the vibrations are taking place in all directions which are perpendicular to the direction of the propagation of the light but in plane polarized light the vibrations are taking place in particular plane in a particular plane that is why it is called plane polarized light.

Now, these vibrations mean the electric vector vibrations and the that is occurring in a plane and so also the magnetic vector, so we are we will take the electric vector as a subject of discussion. So, the electric vector is vibrating in a plane, that is what is called plane polarized light.

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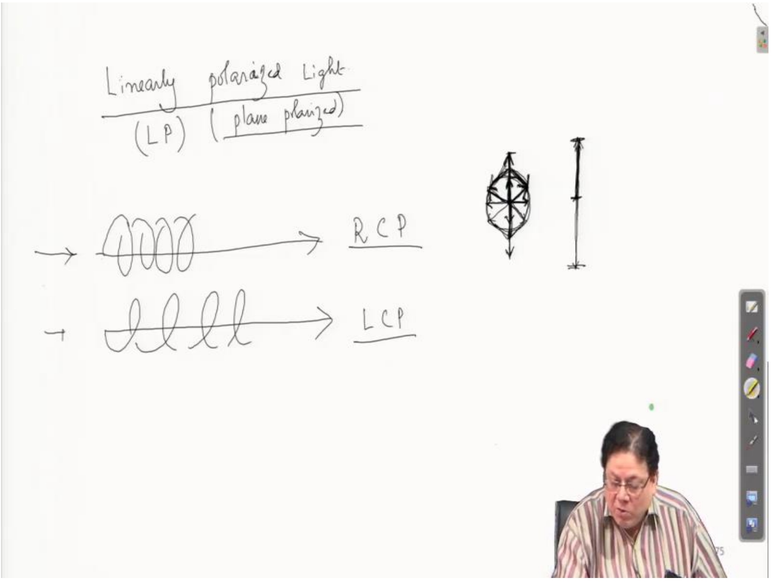

If we go into little deeper the other name of plane polarized light is also is called sorry is what is called linear linearly polarized light, it is same as polarized or abbreviated as LP, this is same as I said our plane polarized light and the plane where the vibrations are taking place by the way is what is called the but this is plane of polarization, plane of polarization.

Actually, what is found that linearly polarized light is nothing but a combination of two circularly polarized light, circularly polarized light means that when light travels from say from here to there this direction, then you can have two components of the light of this linearly polarized light there are two components, and one where the light the electric vector the tip of the electric vector is vibrating and preceding in a clockwise direction.

And that is what is called Right Circularly Polarized light RC Right Circularly Polarized light RCP and that is one component of linearly polarized light, the other component is where the oscillations are taking place in in anticlockwise manner, so that is the left circularly polarized light. So, this is the combination the combination of these two actually makes a plane polarized light.

Remember I have drawn it in a separate lines but actually there super imposed on each other. So, if we now see observed from this direction and take a projection that as light processed, so basically what I am saying the light one light is proceeding like this, this is what is the right-handed helix helical path and so this is what is called right circularly polarized light. And the other one is going in this direction, so this is the left circularly polarized light.

Now, if we take a projection of this a projection view from this side, then what will happen that this will look like that basically the light is the projection will look like a circle, in this circle one component that means the right circular polarized light is going in this direction and the left circularly polarized light is moving in this direction.

So, it is progressing as the light passes a constantly moving and but the projection looks like a circle. So, suppose this is the of the right circularly polarized light that is moving in this direction and this is the left circularly polarized light. So, now both has the if they do not have if they start from the same phase if they are the same phase that means they start at the same point, so if this is the vector this is the vector of the right circularly polarized light, the left circularly polarized light will also have the same amplitude same amplitude of the of the light that means the same size of the vector size will be the same.

So, when they are actually starting from here and then diverging out one goes in this direction and other component goes in the other direction before that the starting point the two vectors are basically align to each other. So, the resultant will be a bigger vector, so this is the amplitude you have started at the starting point, then as they fan out as they diverse to the diverse direction, so what will happen? After some point of time, see this vector will be somewhere here and the vector for the left circularly polarized will be at this point.

And then the resultant will be something, sorry resultant will be something like this, the resultant will take place in the same plane like the earlier vector but what will happen when they started but the amplitude now is less and as the when they are in this at this junction, that means after 90 degree when they cross 90 degree, not cross just at the 90-degree stage, what will happen? This vector will be pointing towards this direction and the other vector pointing towards the other direction, so they cancel out each other.

So, at this point this electric vector amplitude that was highest at the starting point, then it decreased and when they have moved by 90 degree so they will cancel each other so the amplitude is 0, that means your vibration is basically what you started with a high amplitude then the amplitude is decreasing and finally get to 0 and then again when they come at this point suppose they cross the 90 degree, suppose 120 degrees so then you have again a resultant which is exactly the opposite direction to the earlier one and you have this is the your amplitude of the resulting only the direction is reverse now the direction of the vector is reverse now.

So, when they are they have moved by 180 degrees, so then they will add up to each other and they will have the same amplitude like the original starting point only the direction is basically just reversed. So basically, now you are having a vibration that is initially started here that is going down as the light proceeds, then it goes in the (opposite) becomes 0 then again increased in the opposite direction and become the same amplitude as your starting point and then again after this, it starts decreasing it goes in the it decreases again which is 0 and goes in the same direction where it started.

So basically, your vibrations are taking place in the same plain, if you look at this, the amplitude is basically just started from a peak that is the crest and then it goes down and goes reaches the turf and again comes back becomes 0 and then and goes to the highest point. So, that is what is going on as the light travels. So that was all the vibrations are taking place in the same plane, so that is what is the status of a linearly polarized light.

So again, I repeat, a linearly polarized light is nothing but a combination of right circularly polarized light to circular polarized light and one is right circularly polarized, sorry one is right circularly polarized and the other is left circularly polarized, let me erase this and I will read what is written in that in that slide.

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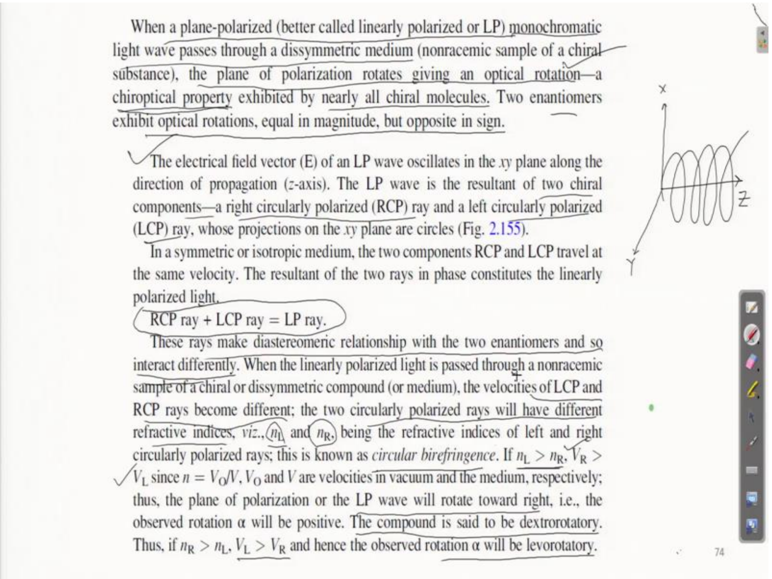

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So, it is said here that when a plane polarized light, which is also called a linearly polarized or LP and it is a monochromatic, so same wavelength passes through a dissymmetric medium, so they have straight gone to the dissymmetric medium, that means a chiral medium, if it passes through a chiral medium, then what happens the plane of polarization gets rotated that is what gives the optical activity and you can measure what is called the specific rotation of a particular dissymmetric media what is symmetric molecule.

Now the plane of polarization rotates giving an optical rotation, that we all know this optical rotation is what is called chiro optical property because chirality is now connected to the light, special form of light, plane polarized or linearly polarized light. So, this property of the showing rotation when plane polarized light passes through a dissymmetric medium is what is called chiro optical property. Exhibited by nearly all chiral molecules, why nearly because some chiral molecules are may have very low rotation, that is one possibility or sometimes they like non resolvable where they go from one form to the other cancelling out the cancelling out the rotation, so that is possible.

To (())(15:02) much we know exhibit optical rotation equal in magnitude but opposite in sign, that is our previous basic knowledge about optically active compounds. Now here it is said what I have said, the electric vector E of an LP web oscillates in the xy plane, so xy plane oscillates in the xy plane provided you have, your let me see whether its oscillates in the xy plane, so if this is suppose x this is your y and this is your it is progressing in this z direction.

So, the light is basically oscillating in the in xy plane which is perpendicular to this z. So, it is going like this, so it is oscillating in the xy plane along the direction of propagation the LP web is the resultant of two chiral components, a right circular polarized light or ray and a left circularly polarized light. Remember, when I talk about circularly polarized, this is basically taking a helical pattern, one ray of light goes in a clockwise direction but in a helical fashion and helix has an inbuilt chirality.

So, this polarize right circularly polarized light it is self-chiral, left circularly polarized light is also chiral. So basically, linearly polarized light is a combination of two chiral entities right and left circularly polarized light and as I have shown that when you superimpose and if you draw that vector diagram, if you draw a projection and then draw the vector diagram you see that the vector oscillates it increases in the highest at the starting point then it goes down to 0 then goes in the opposite direction just like your sinusoidal wave just like a wave.

So basically, we can write that a RCP plus LCP is what makes the linearly polarized ray. Now, because these two rays are itself chiral, so when a linearly polarized light passes through a chiral medium, so what happens? You have a interaction of the right circularly polarized light that is a chiral entity with this chiral medium and you have an entity left circularly polarized light which is interacting with this chiral entity.

So, you have two different interactions, one is right circularly polarized light, one is chiral entity and other is left circularly polarized light but the same chiral entity. So, what is this relationship between these two interactions? They are (())(17:54) relationship because your chiral entity it remains the same, same type of configuration here. So, basically you are having a dash (())(18:05) interaction when between right circularly polarized and the chiral entity and the left circularly polarized and the same chiral entity.

So, that gives the same diastereomeric interaction, so because they have diastereomeric interaction, so there are there are now these two so there are basically this light will have different ultimate the result of that interaction will be different for right and left circularly polarized light. Now, what is the result of this interaction? There are two things that can happen when light passes through a medium, one is absorption the light gets absorbed and another is the light gets slowed down because of higher refractive index as compared to the refractive index in air so light get slow down.

So, basically what happens that either there are two kinds of results you can expect that the slowing down of the velocity of the light, that means reducing the velocity of right circularly polarized light or the left circularly polarized light the amount of reduction of velocity will be different because it is attached to the (())(19:29) relationship and also you can say the absorption the amount of absorption of left circularly polarized light and the right circular polarized light will also be different.

So, these are the two possibilities and that is exactly what happens, the first one when refractive index which actually controls our velocity, so the refractive index of the for the two rays of light when passing through a chiral medium will be different, so one will be higher than the other and that means one ray of light travels faster than the other one, this is what is the phenomena is called this by birefringence circular birefringence it is written here this is what is called circular birefringence I read it here when linearly polarized light, first is important these rays make diastereomeric relationship with the two enantiomers that interactive finally.

When the linearly polarized light is passed through a nonracemic sample of a chiral or dissymmetric compound or medium the velocities of LCP and RCP rays become different the two circularly polarized rays will have different refractive indices that I was mentioning nl for the left circularly polarized light and nr for the right circularly polarized light, these are the two refractive indices.

This is what is known as, that means this difference in the refractive index for the two kinds of rays namely right and left circularly polarized light is what is called circular birefringence. And so, if nl refractive index on a left is greater than refractive index of the right, then we know that as refractive index increases the velocity decreases, so here the velocity of right circularly polarized light will be more than the left.

And it is a vice versa if nl less than nr then Vl will be greater than Vr. So, I will show you because of these difference in velocities the plane of polarization, remember you started with a linearly polarized light with the vibrations taking place the oscillations taking place in a particular plane. So, when there is this differential velocity of the two components, then the plane of polarization actually tilts one way or the other either to the right side or to the left side, that gives actually you something some compounds dextrorotatory some compounds levorotatory.

So, it is all written here that the plane of polarization will rotate now to the right if the velocity of the right circular polarized light is more and it will rotate to the left if the velocity of the left circularly polarized light is more than the right. So, the compound is said to be dextrorotatory when Vr is greater than Vl and when the opposite Vl is greater than Vr the observed rotation will be on the will be on the left side so that will be called levorotatory.

So, this is what is the all about what is linearly polarized light and what it is composed of and then what happens when it travels the chiral medium. Now, remember when you have an achiral medium the interaction is basically enantiomeric interaction with the symmetric medium. So, your absorption will be same amount of absorption for the two kinds of rays will be same, the refractive index will also be same, so there is no question of rotation or there is no question of differential absorption.

And this phenomenon is called circular birefringence that means the difference in refractive index but I told you that the other thing that can happen is difference in absorption extent of absorption that is what is called circular dichroism. So, there are two kinds of effects that can happen, one is circular birefringence that is different refractive index and another is circular dichroism, that means difference differential absorption are the two kinds of rays.

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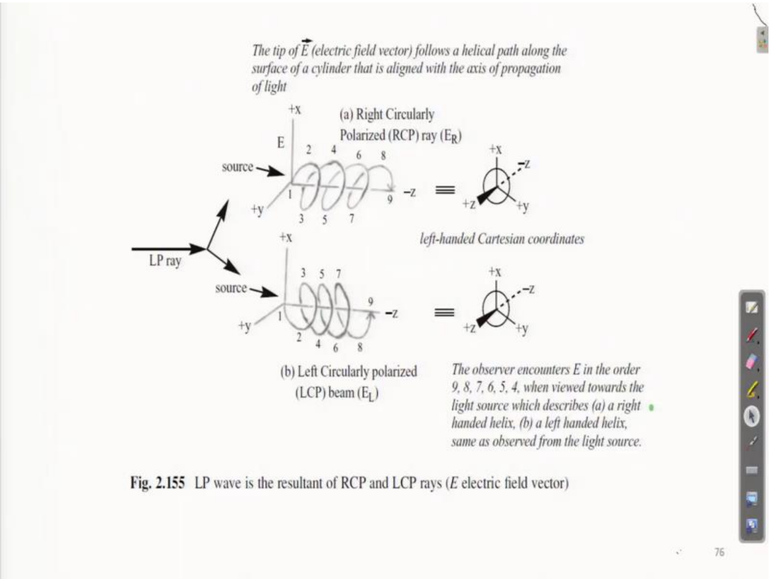

The tip of $\vec{E}$ (electric field vector) follows a helical path along the surface of a cylinder that is aligned with the axis of propagation of light

The observer encounters E in the order 9, 8, 7, 6, 5, 4, when viewed towards the light source which describes (a) a right handed helix, (b) a left handed helix, same as observed from the light source.

Fig. 2.155 LP wave is the resultant of RCP and LCP rays (*E* electric field vector)

I think this I have already shown you that this left and right circular polarized light, let us consider and this is how does it look this circularly polarized light, this is one type of circularly polarized light, this is how the vibrations are taking place the oscillations are taking place.

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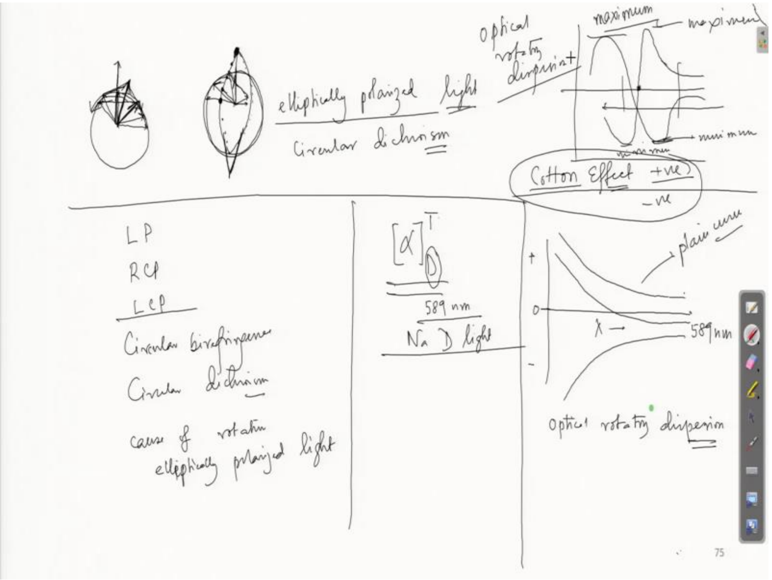

And let us see what happens when it passes through the surfactant diagram, we will try to draw the vector diagram that how this rotation is coming into picture. So, what happens that if it is initially you draw the projection which looks like a circle, so your right circularly polarized light is moving in this direction this is the left circularly polarized light. In a symmetric medium the two components are moving with the same speed or same velocity.

So, what happens when it passes through a chiral medium, suppose the right circularly polarized light is moving faster, so your starting point there at the this is the vector. So, when one of the components moves faster, suppose this and this is still lagging behind this is suppose the vector is at this point, so here the velocity of the right circular polarized light is more than the left that means the refractive index for the right circular polarized light is less than the left circularly polarized light.+

So, the route to the resultant will be something like this. So, the resultant get shifted and that is the reason why you see rotation and the rotation will be more as it passes crosses the medium if it takes if it crosses if the length of the medium is more that means there will be more rotation of this plane of polarization. So basically, what I am saying that supposed then this will come here and that lags behind that is to be here, so again now you have this draw the, so it is now moving towards the right.

So, that is the dextrorotatory case, and levorotatory case is exactly the opposite way the Vl will be more than Vr, so that is the cause of the rotation. And when you have a differential absorption, then what happens the velocity remains the same, this is your starting point velocity remains the same but one is absorbed more than the other, suppose this is observed and that is not observed much the left one.

So, now what will happen they now you have your resultant will be something like this and the resultant will slowly if it moves now here, and this moves up to this point, so the resultant will be something like, it will not be 0 but it will be, so the resultant point I am just putting the points the dots as the value of the resultants.

The result is like this, it was the original point, then the resultant is moving like this so this is how the resultant the tip of the result moves. So basically, it is now following a what is called an ellipe and elliptical path. So this will be this elliptical path. So that is the that is how the light will look like.

So, that is basically happening because of differential absorption. So, the light is said to be now elliptically polarized because it is no longer linearly polarized it is elliptically polarized light. So, you can, so how much is the difference in the absorption that will be reflected by the electricity, electricity of the ellipse of the ellipse that is which is the resultant of this differential absorption because it is now having an elliptical path.

So, earlier it was going in a circular path like this, now it will follow this elliptical path, it is no longer circular and this elliptical path is basically the differential absorption gives the ellipse, then how much is the elliptical pattern which is governed by what is called ellipticity, ellipticity and the like major axis minor axis. And the that will actually vary from compound to compound the amount of ellipticity but this is what is the phenomena of circular dichroism.

So, what we have learnt so far? We have learnt what is linearly polarized, what is right circularly polarized, what is left circularly polarized, then what is circular birefringence, what is circular dichroism and the cause of rotation and cause of elliptically polarized light or elliptically polarized light are generated. So, these are the things that we have discussed. Now, let us consider the circular birefringence which is the cause for giving rotation that the plane of plane polarized light shifts either to the right or to the left.

Now, what happens that usually the you know that a pre compound is a chiral compound is characterized by what is called specific rotation, specific rotation and specific rotation is denoted by alpha D. Now, what is, then have a temperature also because specific rotation is dependent on temperature and the most importantly it is dependent on the wavelength of light that is used to measure the rotation.

Now, this D means actually the 589 nanometer which is also the sodium D light 589 nanometer, so that is our reference that all rotations are measured again sodium D light and at that means at 589 nm. However, since it is dependent on the wavelength, so what happens a question is what happens if you start decreasing the wavelength, suppose this is your original starting point 589 nanometer. So, something has, suppose this is 0 rotation and this is the positive side this is the negative side.

Now, some molecules will have positive rotation, so now you also getting that will be on this side. So, it will generate a curve which will display the variation of rotation against wavelength specific rotation or (())(32:52) rotation against wavelength variation of wavelength. Now, what happens usually if the rotation can increase like this, the rotation can increase like this or if it is a levorotatory compound it can continue to decrease the magnitude continue to increase but if we because it is on the negative side, so it is a will say that it is further going to the negative side, so means it is decreasing.

So, that is usually the case, so and the other thing that may happen is that some molecules start showing levorotation at 589, so the against the D light sodium delight but then it can increase and become dextrorotatory at lower wavelength, that is interesting. If somebody ask you that can a levorotatory compound become dextrorotatory? The answer is possible, if you measure the rotation at another wavelength.

So, there are some compounds which start with levorotation and then as you increase the decrease the wavelength it becomes dextrorotatory or vice versa, starts as a dextrorotatory and becomes levorotatory. So, our dextro and levo is always remember this the reference is the sodium D light and so that is a basis for describing some molecules dextro and levo. So, this is what happens when the rotation versus wavelength gives like this type of graph this is what is this variation is what is called optical rotatory dispersion, this is one aspect.

The other aspect is this is what this curve is what is called plane curve. Now this type of curve for a chiral compound is observed if you are observing the rotation within a wavelength range which falls outside the wavelength of absorption because molecules absorb light because they have chromophores now whether they have strong chromophores or weak chromophore or at what wavelength they will absorb it all depends on the type of bonds that it has, whether it is a pi bond or its a sigma bond, sigma sigma star absorption you are talking about or transition sigma sigma star or pi pi star or n pi star all these are possibilities.

So, this type of plane curve is observed when you are measuring the rotation against wavelength but this wavelength range falls outside the absorption range for that chiral molecule. So, the question is what happens then if it is a if you are measuring the rotation at the at the wavelength or near the vicinity of the wavelength, vicinity of the wavelength what happens to the rotation? What happens to this curve? How the rotation varies with the wavelength when the wavelength is at the absorption region.

This is interesting, what happens here that we see what is called an anomalous curve, that means the as you decrease the wavelength as I said initially you can have increase or decrease depending on the nature of the compounds, suppose it is increasing but suppose this is your wavelength of absorption, that means the molecule is observing the light at this in this region because you know UV spectroscopy absorption and leading to electron transition, electron transition takes place in a narrow window.

So, when you enter into that window where absorption is taking place, then what happens that the sometimes the absorption goes up and then goes down and them again goes up. So, this type of graph you can see, that means what is happening that for some chiral compounds as you are measuring the rotation near the or within the vicinity of the absorption window, then or within the absorption window not vicinity within the absorption window, then what happens you get what is called an anomalous curve.

Anomalous curve is basically that the rotation increases which is the maximum value and then goes down and this is exactly where the rotation is 0, that means both the refractive indices becomes equal at that point for the left and right circular polarized light and then it goes down and reaches a minima and then again goes up, this is one type of scenario.

The other type of scenario is basically is could be the that you can have first a minima then a maxima and then again it goes down. So this is a minimum followed by a maximum in both the cases you are getting anomalous curve for any chiral compound you will get an anomalous curve in the window where it is absorbing window of wavelength where it is the molecule is absolving.

And so, two types of carbon can generate anomalous curve that in one possibility is that you first get a maxima followed by a minima or it is the other way around. So, this is now this is what is called anomalous behavior and this is what is called the molecule is showing what is called the cotton effect, cotton effect is this basically the anomalous curve but it has been given a sign depending on whether the maxima is followed by a minimum or a minima is followed by a maxima.

Remember, here we are decreasing the wavelength as we decrease the wavelength, if the maximum comes first followed by minimum, that is what is called positive cotton effect and if it is minima followed by maxima, then that is called a negative cotton effect. Now, this is very important this is the phenomena which is also known as optical rotatory dispersion optical rotatory dispersion, as I told you optical rotatory dispersion is basically the variation of the rotation against wavelength.

Now there are two types of dispersion you can see, one is the occurrence of the plane curve which takes place outside the window of absorption and within the window of absorption you get this anomalous curve, both are optical rotatory dispersion but when you get the anomalous curve you have the cotton affect either positive cotton affects or negative cotton affect. So, the next lecture will start from this cotton effect and we will discuss how the sign of cotton effect helps one to get to the configuration or confirmation of a molecule of a chiral molecule. Thank you very much.