UNIT 4: ORD and CD

(Part II: Interaction of Polarized light with Optically Active Matters)

M.Sc. Semester II

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CONTENT:

- Absorption and Dispersion
- Optical Activity
- Optical Rotatory Dispersion
- Circular Dichroism

Absorption and Dispersion

- **Dispersion** is the wavelength dependence of refractive index. That is, a curve of refractive index of a substance vs. wavelength of the incident radiation is known as a *dispersion curve*.

- It indicates how light of various frequencies would be dispersed by a prism made of the substance in question.

- When light travels from a vacuum into another medium, its frequency remains constant but its velocity and its wavelength are reduced. The index of refraction of the medium (n_{medium}) is defined as:

$$\boxed{n_{medium} = \frac{c_{vacuum}}{c_{medium}} = \frac{\lambda_{vacuum}}{\lambda_{medium}}} \qquad \text{……(1)}$$

Absorption and Dispersion

- ***Absorption*** is the reduction of the intensity of incident light (I_o) as it passes through a substance.
- The wavelength dependence of the absorption of light of different frequencies by a substance is known as its absorption spectrum.
- This absorption increases exponentially with increasing distance travelled in the medium, and, for solutions, with increasing concentration of the solute, according to the equation:

$$I = I_o(10^{-\varepsilon cl}) \qquad \text{……(2)}$$

where I is the intensity of the transmitted light, c is the molar concentration, l the path length, and ε the molar extinction coefficient (a characteristic of the substance).

Spectroscopic Methods for determination of Absolute Configuration of Coordination Complexes

The absolute configuration of complexes can be determined by

(i) Optical Rotatory Dispersion (ORD)

(ii) Circular Dichroism (CD)

These methods depend on the behaviour of polarized light passing through a solution (usually) of the optically active compound. The results have to be interpreted by comparison with a similar compound of known as ***Absolute configuration.***

Optical Rotatory Dispersion (ORD)

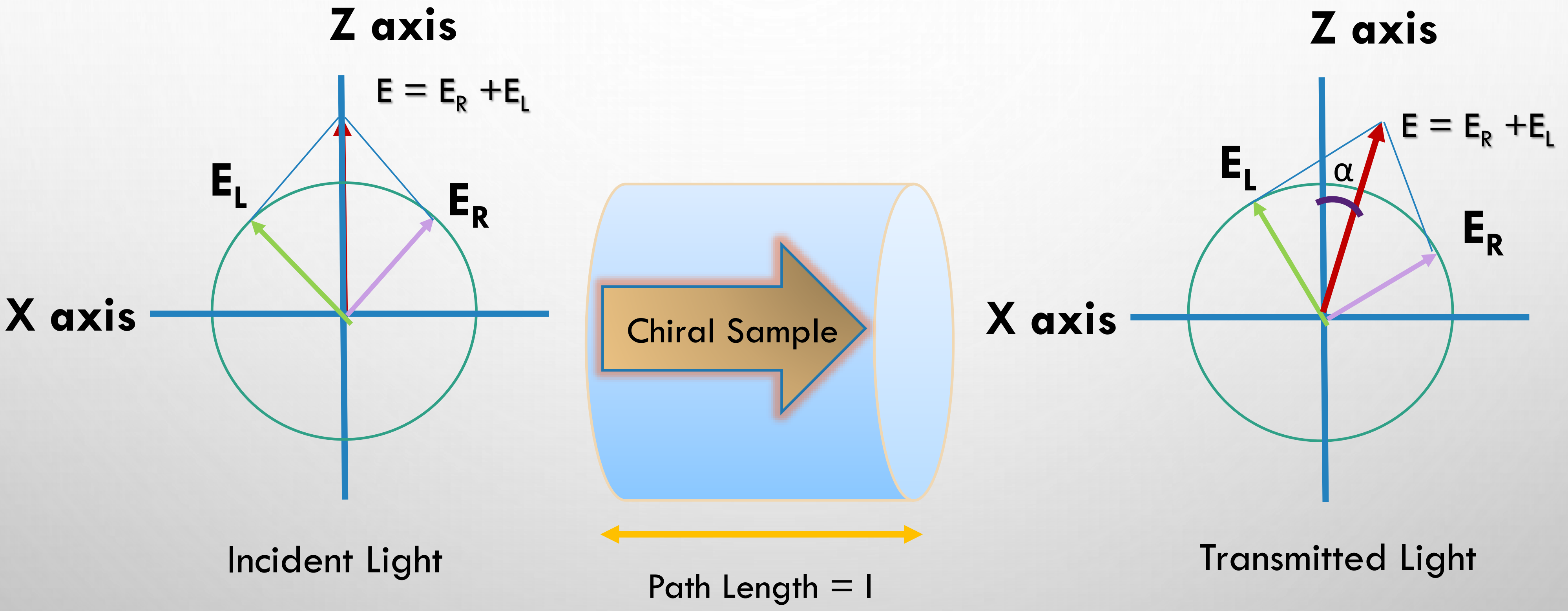
The rate of change of specific rotation with respect to wavelength is known as **Optical Rotatory Dispersion** (ORD).

As we already seen in *part I* that plane polarized light can be regarded as and experimentally broken down into two circularly polarized components, equal in amplitude but opposite in rotation.

An optically inactive substance will retard the speeds of two circularly polarized components to the same extent, with no net rotation.

However, the speed of the circularly polarized components are retarded by an optically active substance to different extent resulting in the rotation of plane of polarization.

Optical Rotatory Dispersion (ORD)



Optical Rotatory Dispersion (ORD)

The rotation of plane of polarization by an optically active medium is the result of unequal angles which E_L and E_R make with Z axis.

It has been shown that since the speed of light in a medium is manifested in the refractive index of the medium, essential property of an optically active substance is that it has different refractive indices for the left and right circularly polarized light, n_L and n_R, respectively.

This is also the reason why an optically active substance is said to be "circularly birefringent."

Circular Birefringence

The difference in indices of refraction for right circularly polarized light (RCP) and left circularly polarized light (LCP) is known as *circular birefringence*.

Thus, on passing plane polarized light (PPL) through optically active compound results in an unequal rate of propagation of right and left circularly polarized rays due to circular birefringence.

This unequal rate of propagation for both right and left circularly polarized light deviate the PPL from its original direction and it is called ***optical rotation***.

Upon emerging from the medium, the resultant beam is still *linearly polarized*, with its plane of polarization having been rotated by an amount $\boldsymbol{\alpha}$.

Optical Rotation

- If the path length of the beam in the optically active is represented by l, then, the wavelengths of the two beams of circularly polarized light are given as:

$$\boxed{\lambda_L = \frac{\lambda_{vac.}}{n_L}} \quad \& \quad \boxed{\lambda_R = \frac{\lambda_{vac.}}{n_R}}$$

$$n_{med.} = \frac{c_{vac.}}{c_{med.}} = \frac{\lambda_{vac.}}{\lambda_{med.}}$$

……(1)

Number of full waves (E_L and E_R) present in the distance l:

For E_L, $$\frac{l}{\lambda_L} = \frac{l.n_L}{\lambda_{vac.}}$$ ……(3)

For E_R, $$\frac{l}{\lambda_R} = \frac{l.n_R}{\lambda_{vac.}}$$ ……(4)

Optical Rotation

The difference in the number of waves is therefore,

Equation…… (3)-(4)

$$\frac{l(n_L - n_R)}{\lambda_{vac.}}$$

And the **phase difference** = 2π x difference in the number of waves

$$= 2\pi \frac{l(n_L - n_R)}{\lambda_{vac.}}$$

Optical rotation (α) = Phase difference/2

*Any linearly polarized state at an angle θ is the superimposition of right and left circularly polarised components with a relative phase difference of 2θ.

So, **Optical rotation (α) =** $\frac{\pi\, l\, (n_L - n_R)}{\lambda_{vac.}}$

Optical Rotation

Spectropolarimeters are the polarimeters used to make measurements at a variety of wavelength; they record ‘α’ as a function of λ at a specific temperature **T**. At a specified wavelength; optical rotation ‘α’ is called as specific rotation, $[\alpha]_{\lambda}^{T}$,

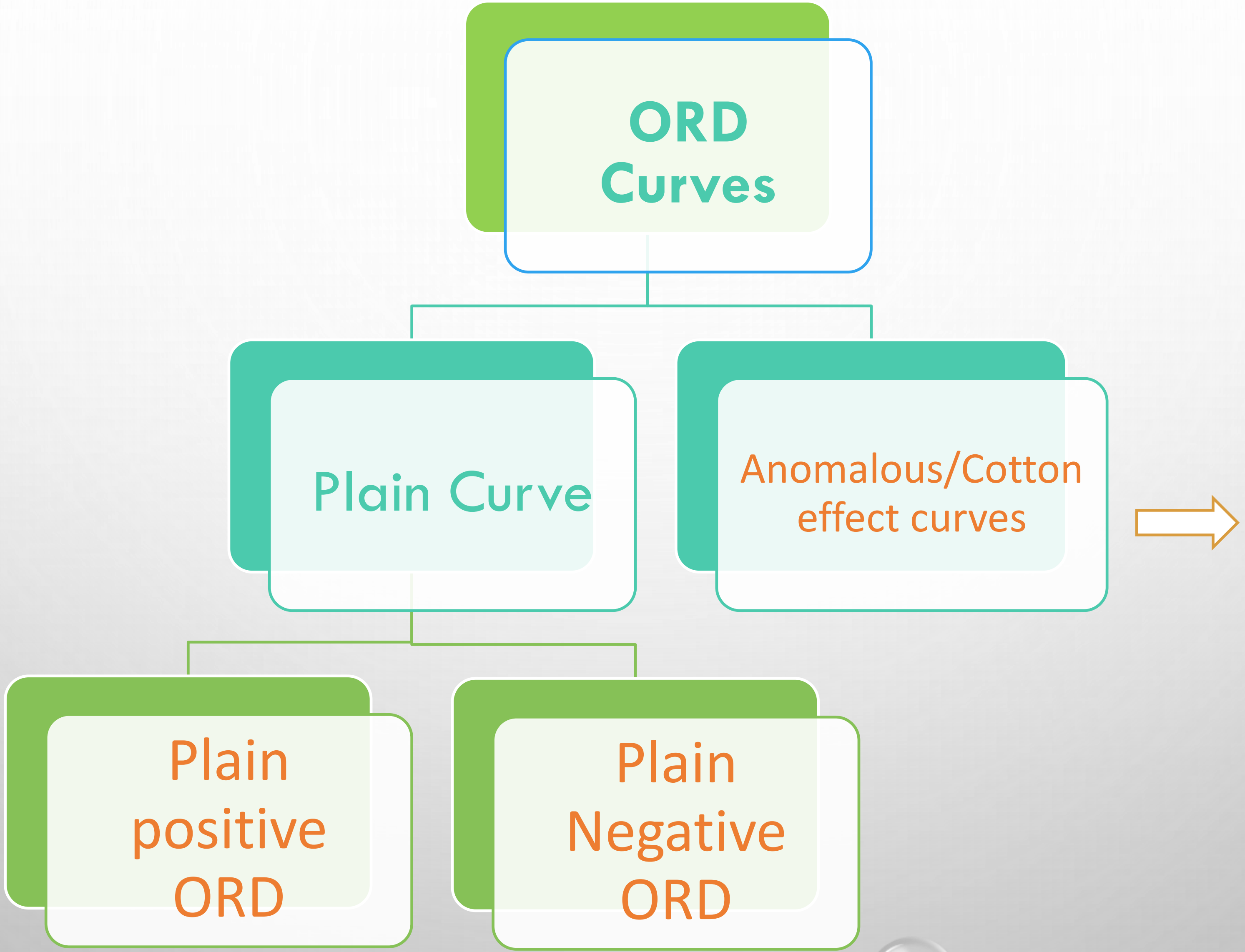
$$[\alpha]_{\lambda}^{\mathrm{T}} = \frac{\alpha}{l \text{ x } c}$$

Where ***α*** is the observed rotation at wavelength *λ* in degrees, ***l*** is the light path in decimeters, ***c*** is concentration of the optically active substance in grams per ml.

For ORD we commonly we use molar rotation $[\mathrm{M}]_{\lambda}$ (unit: °cm^{2}/dmol) which is defined as: $[\mathrm{M}]_{\lambda} = \frac{M\alpha}{100l\, c}$

Where, M is the molecular weight in grams per mol.

- *ORD curve is a plot of specific rotation, [α] vs λ or molar rotation [M] vs λ.*



ORD Curves

Plain Curve

Anomalous/Cotton effect curves

Plain positive ORD

Plain Negative ORD

Explained letter in this chapter

Plain Curve

- These curves don’t contain any peak or inflections (maximum or minimum) and these don’t cross the zero rotation line.

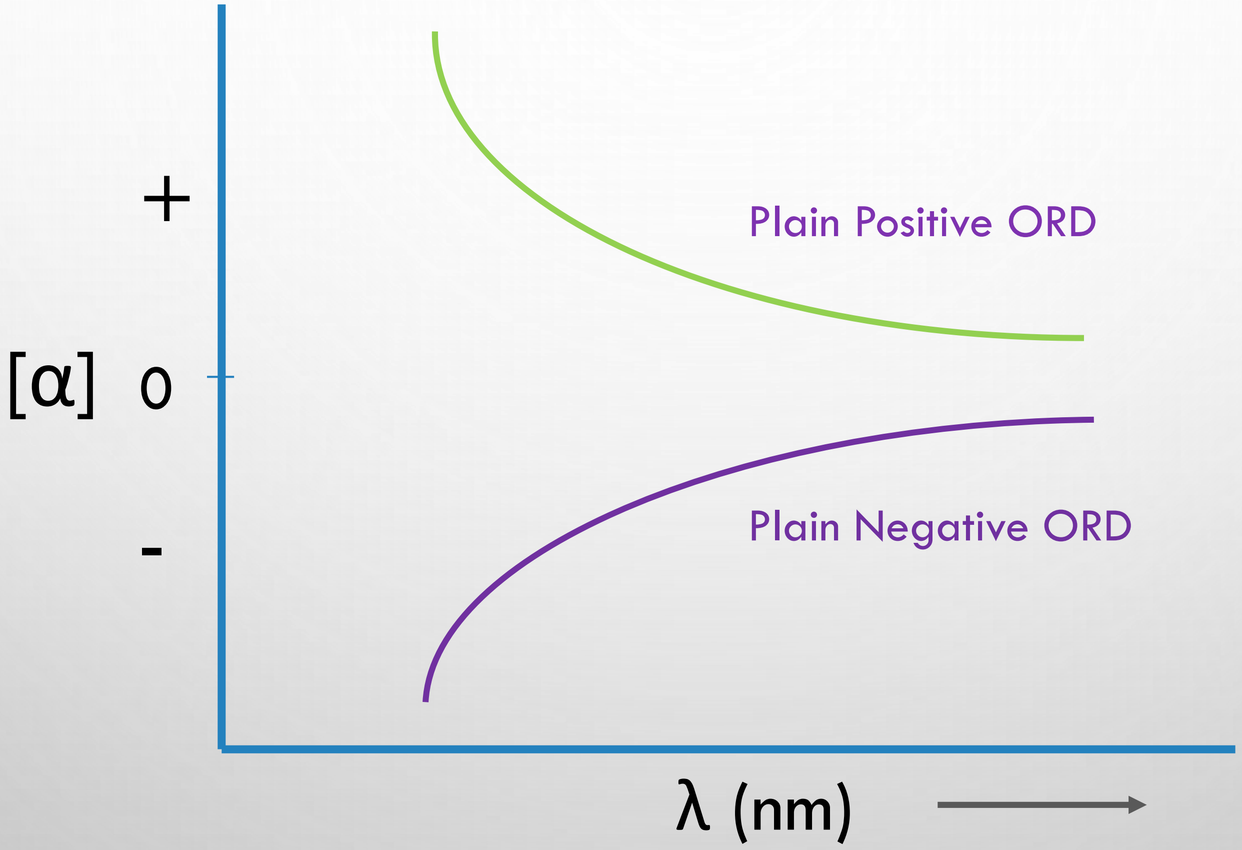
Plain positive ORD

- Plain positive ORD curves are obtained when specific rotation increases with decreasing wavelength. In other words, clockwise rotation is plotted positively.

Plain negative ORD

- Plain negative ORD curves are obtained when specific rotation decreases with decreasing wavelength. In other words, counter clockwise rotation is plotted negatively.

Plain Curve ORD



Circular Dichroism

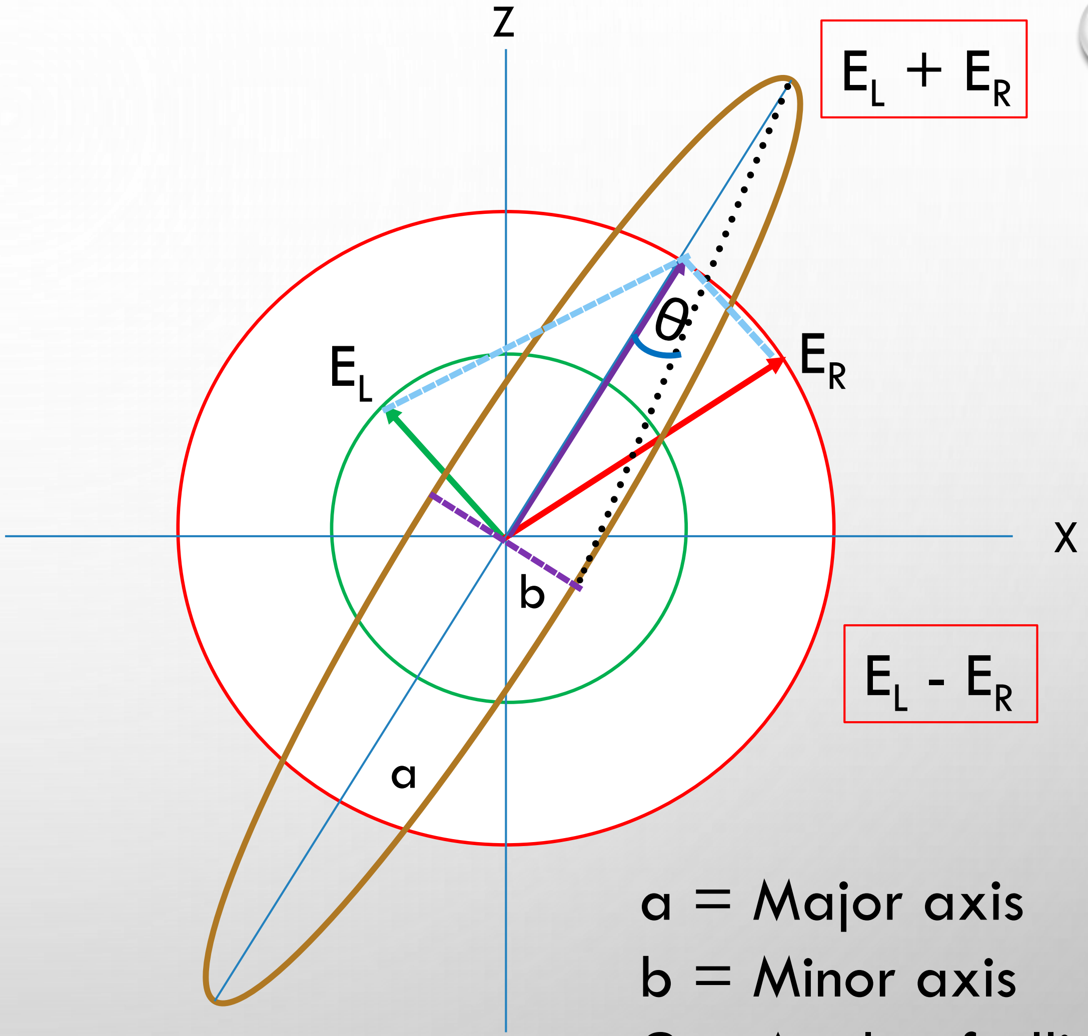
- Optical *circular dichroism* (CD) is the differential absorption by a medium of right and left circularly polarized light.

Optically active compounds possess this special property of absorption of the left-handed circularly polarized light to a different extent than the right-handed circularly polarized light. This phenomenon is called the circular dichroism.

The electric field of a light beam causes linear displacement of charge upon interaction with a molecule, whereas its magnetic field causes a circulation of charge. These two motions collectively results in a helical displacement when light impinges on an optically active molecule (both field vectors in the same place are of same direction but at different moments of time).

Circular Dichroism

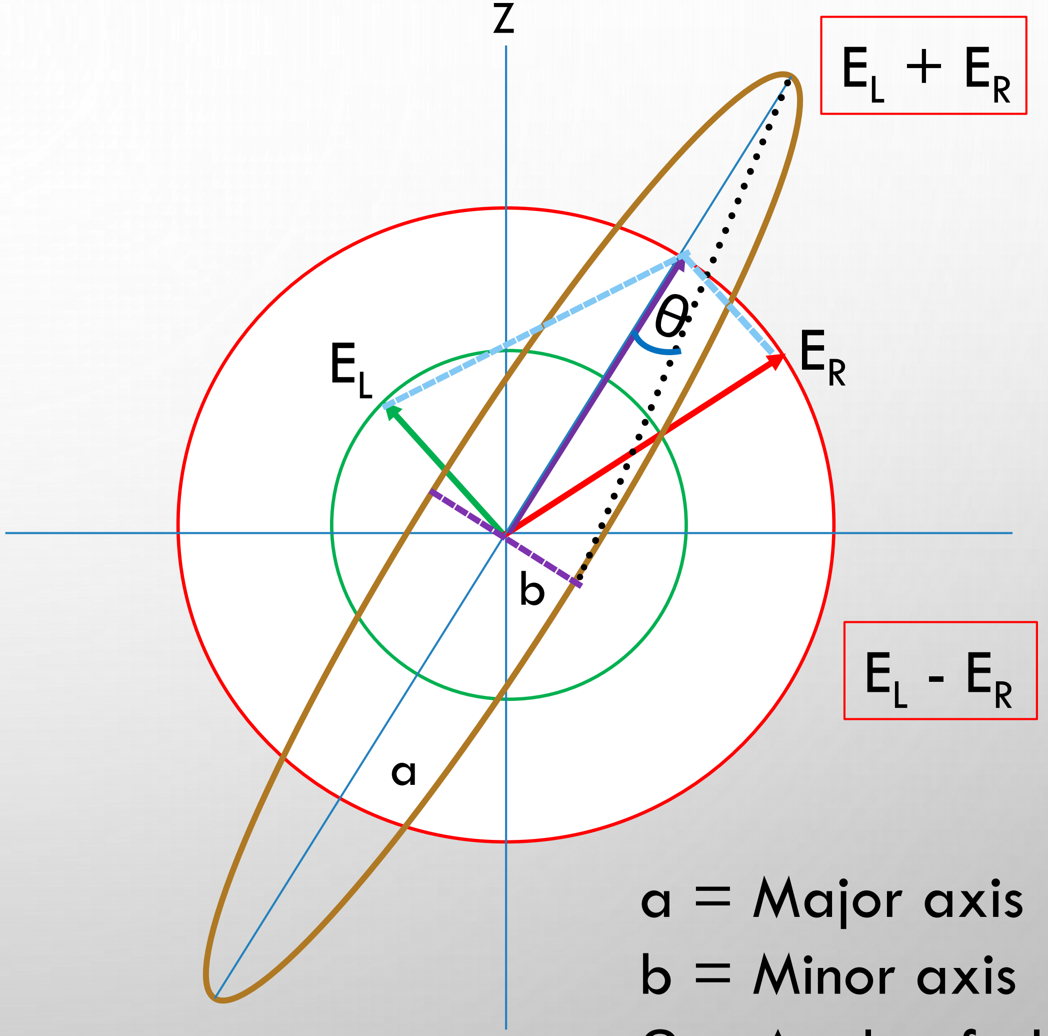
If the absorption is different for right and left handed circular-polarized light then the linearly polarized light will become elliptically polarized. The elliptical polarized light (Brown) is shown in figure, which is composed of unequal contributions of left (green) and right (Red) circular polarized light. The ellipticity (θ) of light is defined by the arc tangent of the ratio of major axis to the minor axis of transmitted light.



a = Major axis
b = Minor axis
Θ = Angle of ellipse

Circular Dichroism

Notice that the major axis of the ellipse is parallel to the polarization plane of the original light wave. This is always the case, regardless of which circular component is absorbed to greater extent by the medium. But the direction of rotation of elliptically polarized light (or, more exactly, its field vector) is determined by the circular component that remains stronger after traversing the material. In this case, the field vector of elliptically polarized light rotates in the same direction as that of the component shown in red colour, which traverses through the medium with comparatively higher intensity.



a = Major axis
b = Minor axis
ϴ = Angle of ellipse

Circular Dichroism

The quantities in CD are Δε (the difference in molar absorptivity)

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R \neq 0$$

The angle of ellipticity (θ) is defined as:

$$\theta = \frac{\pi(\kappa_L - \kappa_R)}{\lambda}$$

and

$$tan\theta = \frac{E_R - E_L}{E_R + E_L}$$

Where, κ (kappa) is the absorption index, it is related to absorption coefficient ***K*** by equation

$$K = \left(\frac{4\pi}{\lambda}\right)\kappa$$

θ has the units in radians/cm and can be converted from radians to degree by multiplying by 180/π.

$$\theta = \frac{180(K_L - K_R)}{4\pi}$$

Circular Dichroism

Now the molar ellipticity of the sample is given by

$$[\theta] = \left(\frac{\theta}{cl}\right)\left(\frac{M}{100}\right)$$

where, c is the concentration in moles/litre, l is path length in cm, and θ is the measured ellipticity.

In terms of extinction coefficients where, K=2.303εc, the equation can be rewritten as:

$$[\theta] = 3300(\Delta\varepsilon)$$

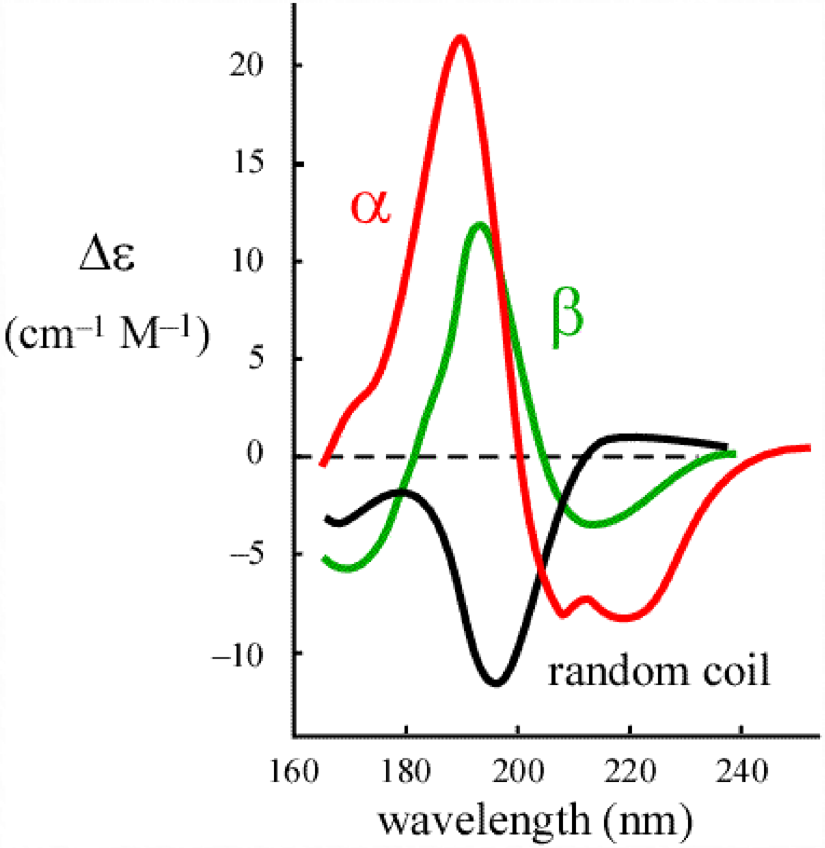
Δε = Circular Dichroism

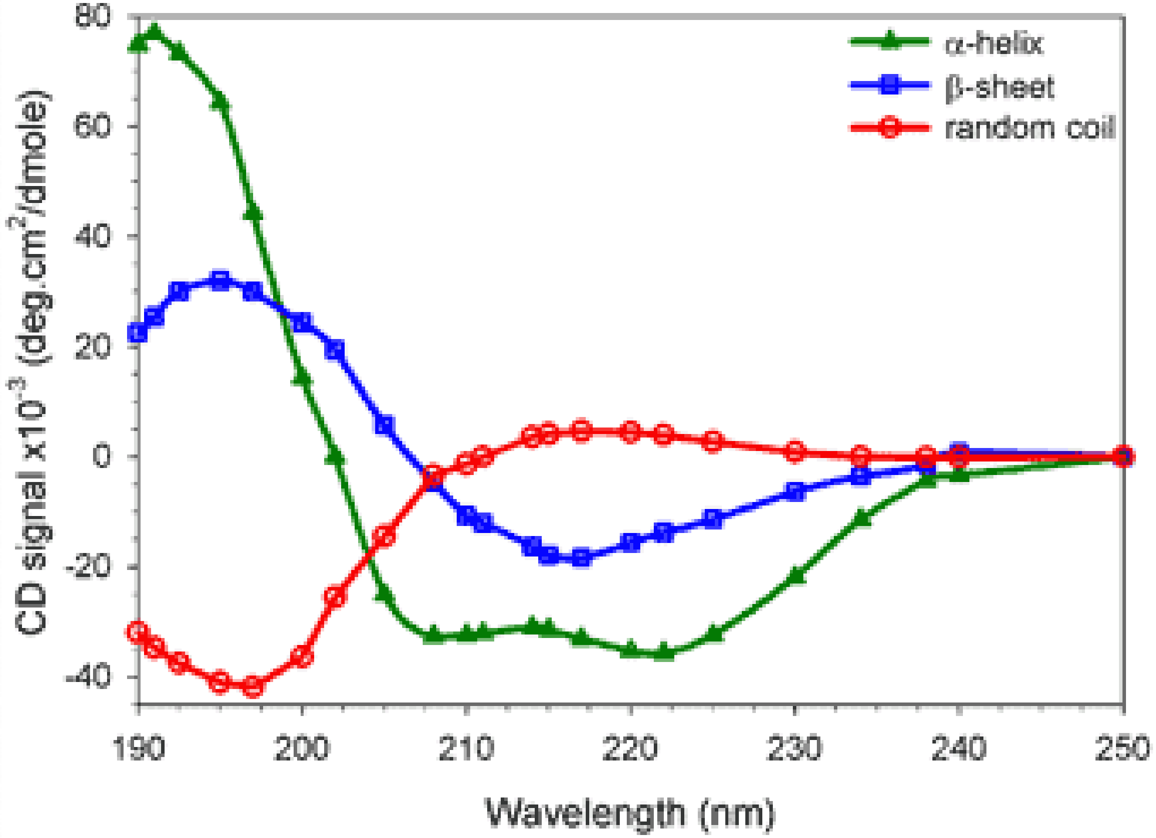
All optically active compounds exhibit CD in the region of appropriate absorption band. CD is plotted as $\varepsilon_L - \varepsilon_R$ vs λ.

CD is measured as a quantity called mean residue ellipticity [θ], whose units are degrees-cm^2/dmol.

Circular Dichroism Curves

CD is measured as a quantity called mean residue ellipticity [θ], whose units are degrees-cm^2/dmol.





*Adopted from internet sources

Reference:

1. S. Kirschner, The Optical Rotatory Dispersion and Circular Dichroism of Coordination Compounds, *Coordin. Chem. Rev., 2 (**1967**) 461-494*.
2. Module 25: Spectroscopic methods for determination of Absolute Configuration of Coordination Complexes, e-pathshala.

THANK YOU

Next.....
Part III: Cotton effect, Faraday and Kerr effects