

OPTICAL ROTATORY DISPERSION (ORD)

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The bottom of the slide features a series of horizontal bars in shades of teal and light blue, creating a modern, layered design.

Overview:

- Introduction
- Fundamental Principles of ORD
- Circular Dichroism
- Instrumentation
- Cotton Effect
- Applications of ORD and CD
- Specific applications of ORD
- References

Introduction

- **Optical rotatory dispersion** is the variation in the optical rotation of a substance with a change in the wavelength of light.
- Optical rotatory dispersion can be used to find the absolute configuration of metal complexes.
- For example, when plane-polarized white light from an overhead projector is passed through a cylinder of **sucrose solution**, a **spiral rainbow** is observed perpendicular to the cylinder.

Introduction



Introduction

- **Chiral molecules** exhibit circular birefringence, which means that a solution of a chiral Substance presents an anisotropic medium through which left circularly polarised (L-CPL) & Right circularly polarised (RCPL) propagate at different speeds.
- This leads to **optical rotation** which is measured by using a polarimeter.
- Measuring optical rotation as a function of wavelength is termed **Optical rotatory dispersion (ORD) spectroscopy**

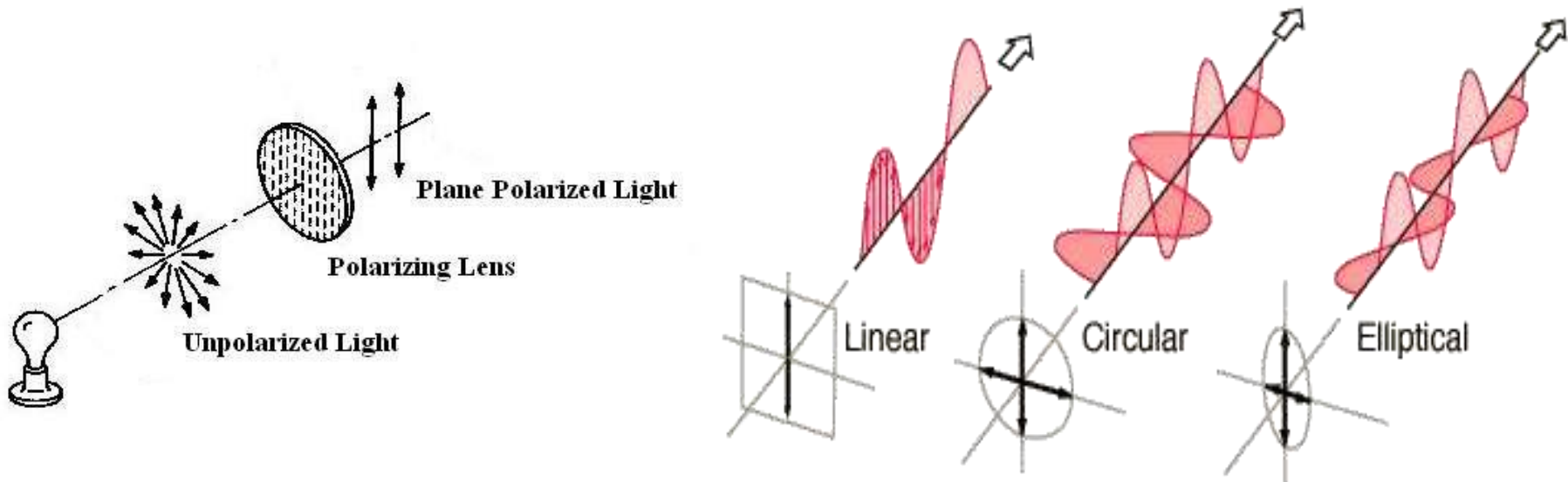
FUNDAMENTAL PRINCIPLES OF ORD:

- Plane/Linearly polarized light.
- Optical activity.
- Specific rotation.
- Circular Birefringence/Optical Rotation

FUNDAMENTAL PRINCIPLES OF ORD:

Plane/linearly polarized light

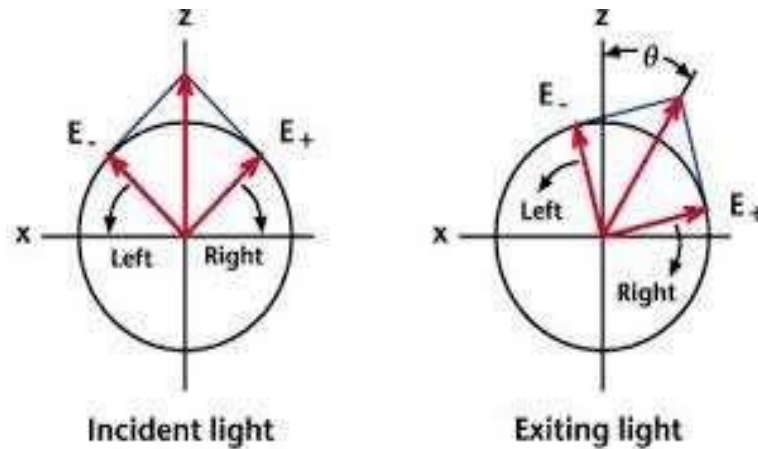
- Light from ordinary lamp consists of waves vibrating in many different planes. When it is passed through polaroid lense it is found to vibrate in one plane is said to be plane polarised light or polarised light.



FUNDAMENTAL PRINCIPLES OF ORD:

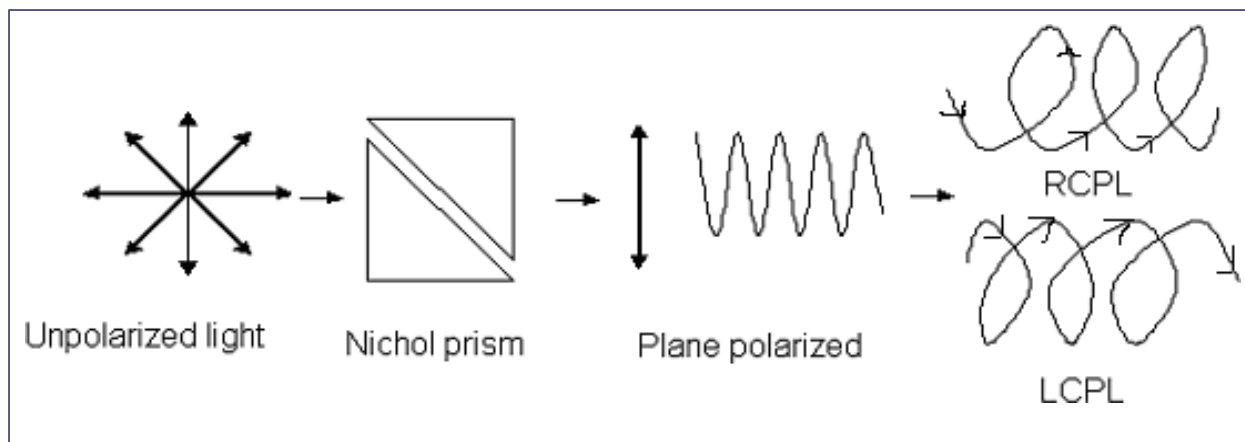
Optical activity

- The compounds which are having the ability to rotate the plane of polarised light are called **Optically active compounds**.
- This property of compound is called **optical activity**. It is measured by Polarimeter.



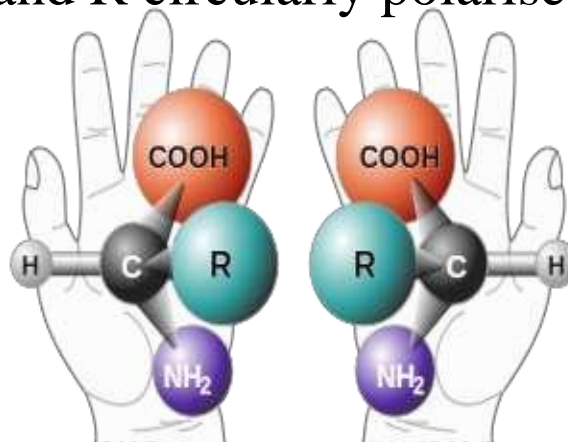
FUNDAMENTAL PRINCIPLES OF ORD:

- Compound which rotates plane of polarised light to right (clockwise) is called **DEXTROROTATORY** & is denoted by (+) sign. If the compound rotates plane of polarised light towards left side (anti clockwise) is called **LEVOROTATORY** & is denoted by (-) sign.



FUNDAMENTAL PRINCIPLES OF ORD:

- **Enantiomers** are optically active compounds. Optically active molecules have different refractive indices, and different extinction coefficients for L and R circularly polarised light.



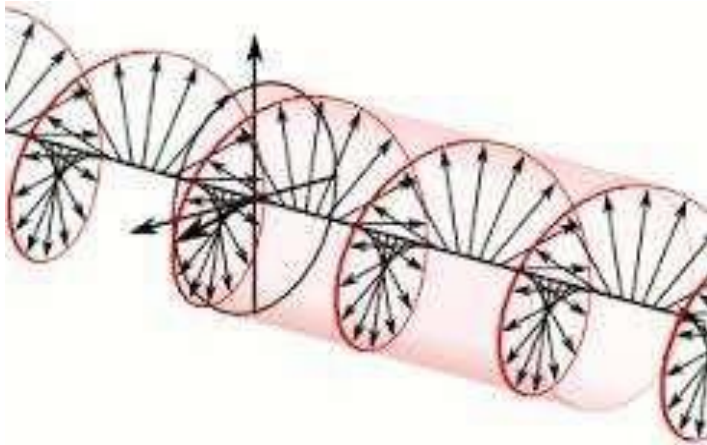
For a compound to be optically active it must be devoid of the following properties –

1. Plane of symmetry (σ)
2. Center of symmetry (i)
3. Alternating rotation – reflection axis of symmetry or an improper axis (s)

FUNDAMENTAL PRINCIPLES OF ORD:

Rotation of plane polarized light(FRESNELS EXPLANATION):

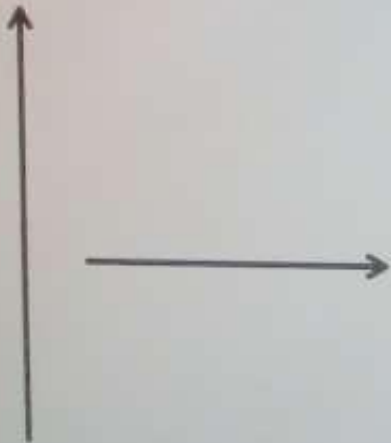
- According to Fresnel, a plane polarized light may be considered as the combination of two circularly polarized light of which one is right circularly polarized light (RCPL) & other is left circularly polarized light (LCPL) which are in equal & opposite in nature.



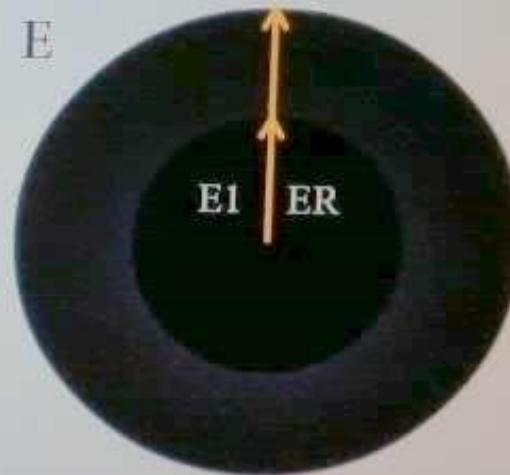
RCPL+LCPL = Plane
Polarized light (PPL)

FUNDAMENTAL PRINCIPLES OF ORD:

THE FIGURE BELOW REPRESENTS HOW THE ELECTRIC VECTOR OF RCPL (E_R) & THAT OF LCPL (E_L) COMBINED TO GIVE A PLANE POLARIZED WAVE (E)



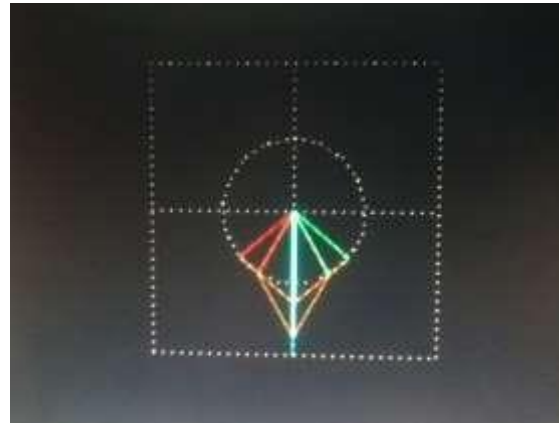
Plane of polarization



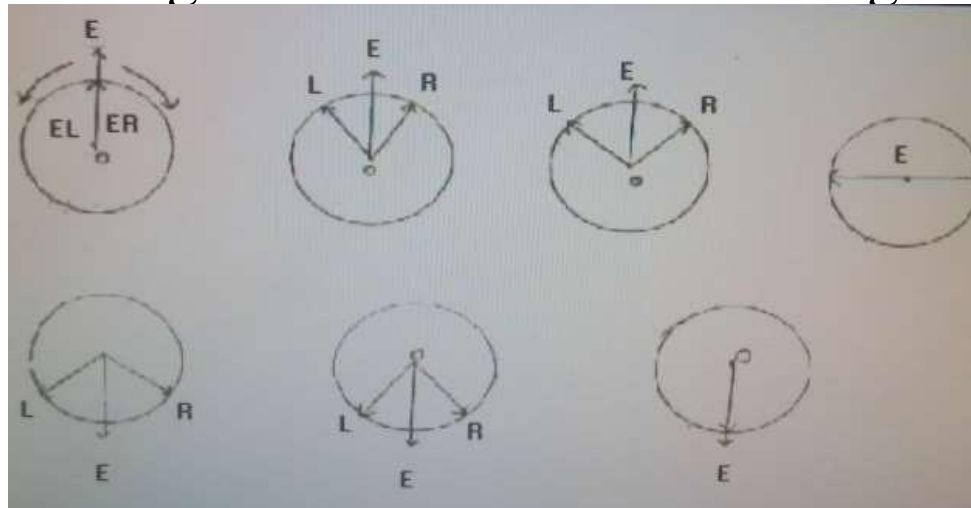
$RCPL + LCPL = PPL$

FUNDAMENTAL PRINCIPLES OF ORD:

- If Refractive index is same for two circularly polarized light then it vibrate in opposite direction with the same angular velocity.



- In the below image we can observe the change of E



FUNDAMENTAL PRINCIPLES OF ORD:

Specific rotation

- It is defined as the observed angle of optical rotation α when plane-polarized light is passed through a sample with a path length of 1 decimeter and a sample concentration of 1 gram per 1 milliliter.

$$[\alpha]_{\lambda}^T = \frac{\alpha}{l \times d}$$

Where,

α – Angle of Rotation in degrees

l – path length is in decimeters

d – Density of liquid is in g 100/ml

T – Temperature.

FUNDAMENTAL PRINCIPLES OF ORD:

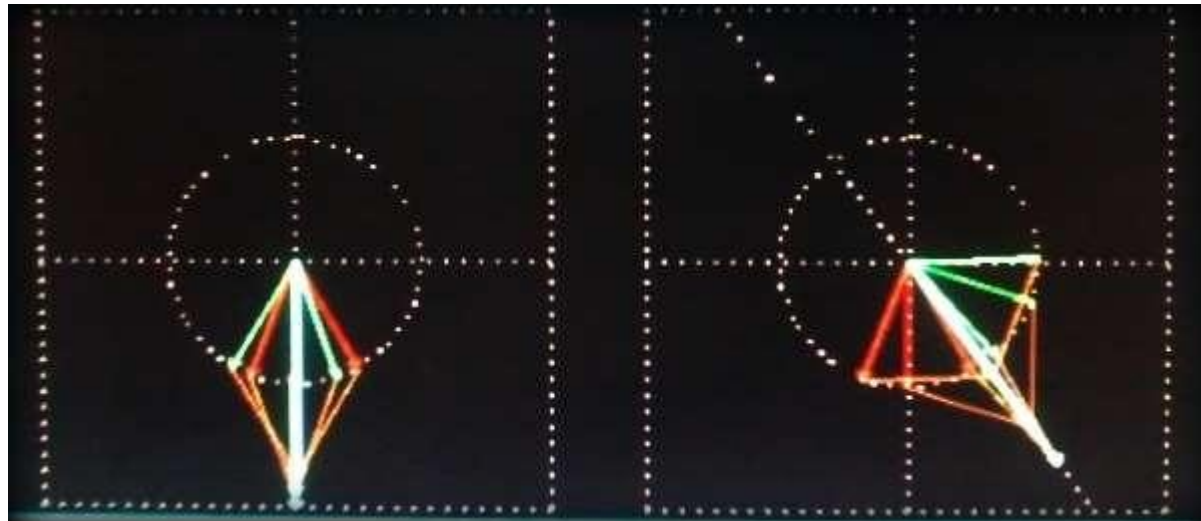
It depends on various factors like:

- Nature of substance.
- Length of the column.
- Concentration. of the solution
- Temperature of the sol.
- Nature of the solvent.
- Wavelength of the light used.

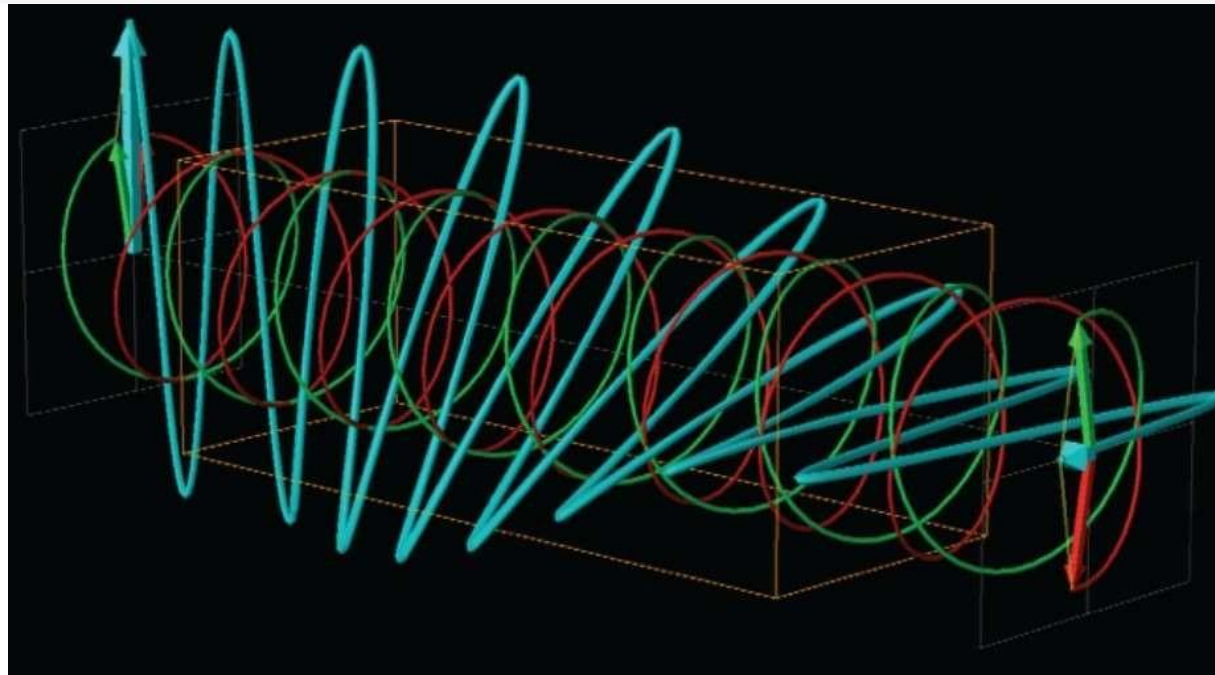
FUNDAMENTAL PRINCIPLES OF ORD:

Circular birefringence/Optical rotation:

- Circular Birefringence is the difference in refraction (and the associated speed of light) of left and right circularly polarized light.
- The polarization plane of linearly polarized light traversing a Circularly Birefringent medium is rotated.



FUNDAMENTAL PRINCIPLES OF ORD:



- The **rotation** is the result of an increment in the relative phase of the left and right circularly polarized components in which the plane polarized light can be decomposed.
- The increment (which can be either positive or negative) is caused by differences in the interactions of left and right circularly polarized light with a medium consisting of **chiral molecules**.

FUNDAMENTAL PRINCIPLES OF ORD:

- Optical rotation caused by compound changed with wavelength of light was first noted by **Biot** in 1817.
- The rotation angle is given by

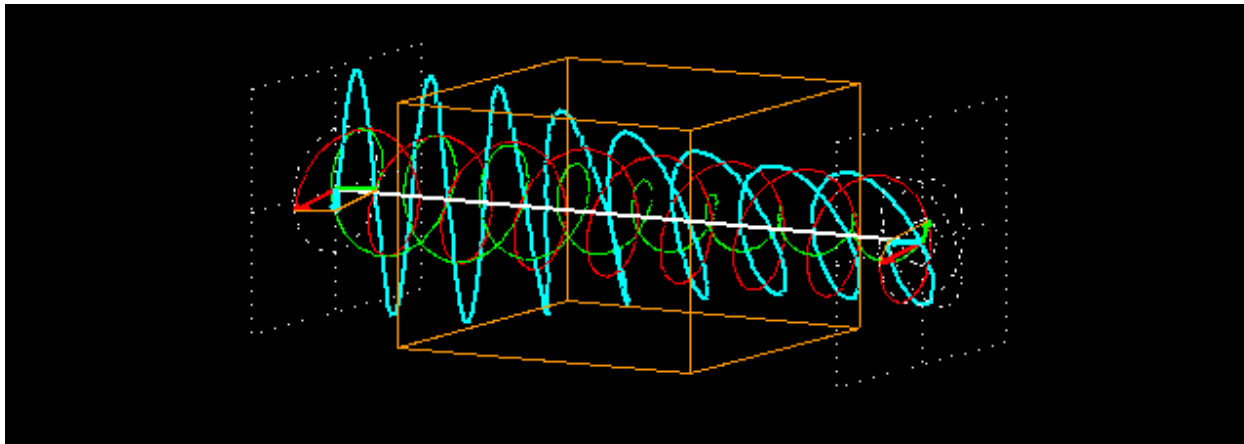
$$\alpha = \pi l (n_L - n_R) / \lambda$$

Where,

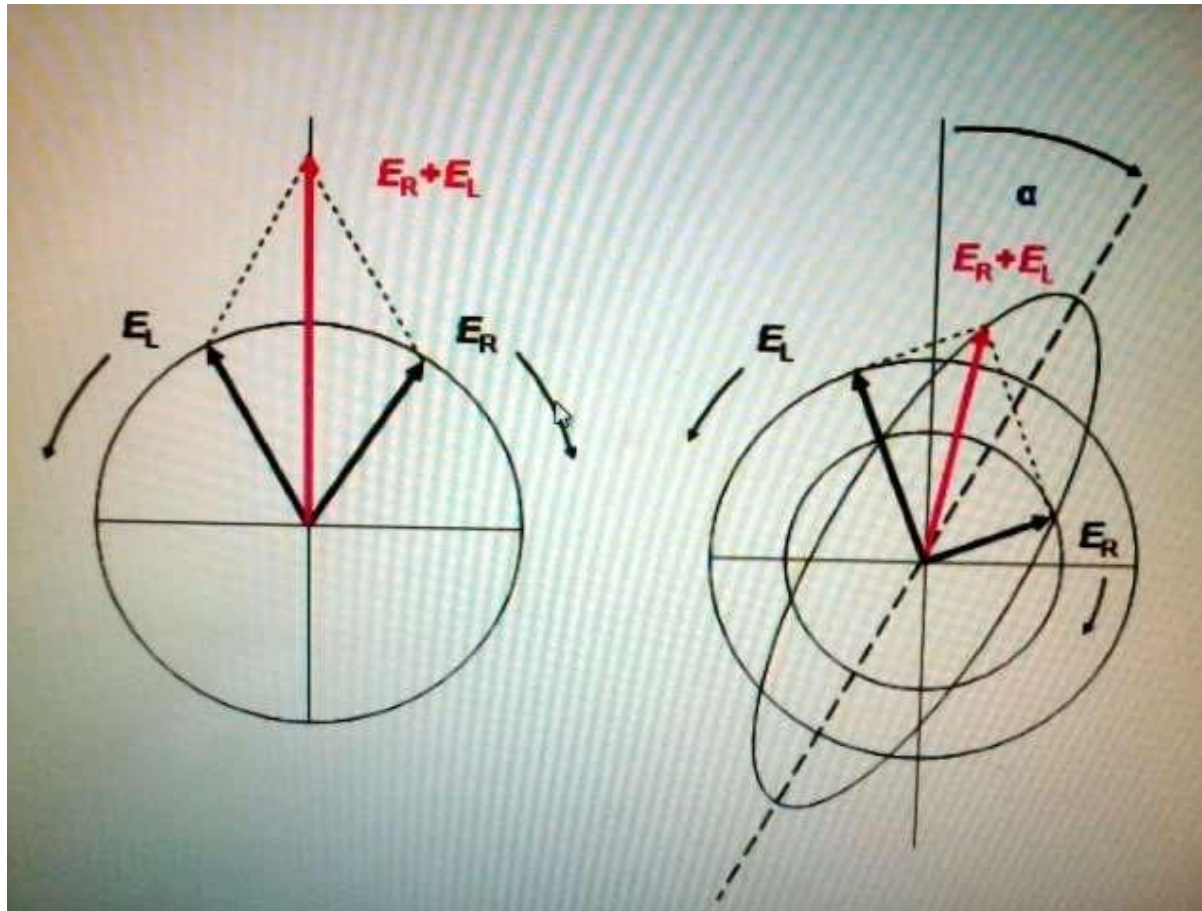
l is the path length traversed by the light
 n_L and n_R are the Refractive Indices for left and right circularly polarized light of wavelength

Circular Dichroism

- Some materials possess special properties of **absorption** of the left circular polarised light to different extent than the right circularly polarised light.
- When the component emerges out there is an imbalance in their strength & the resultant two will not be linearly polarized but elliptically polarized & this phenomenon is called as **CIRCULAR DICHOISM**.



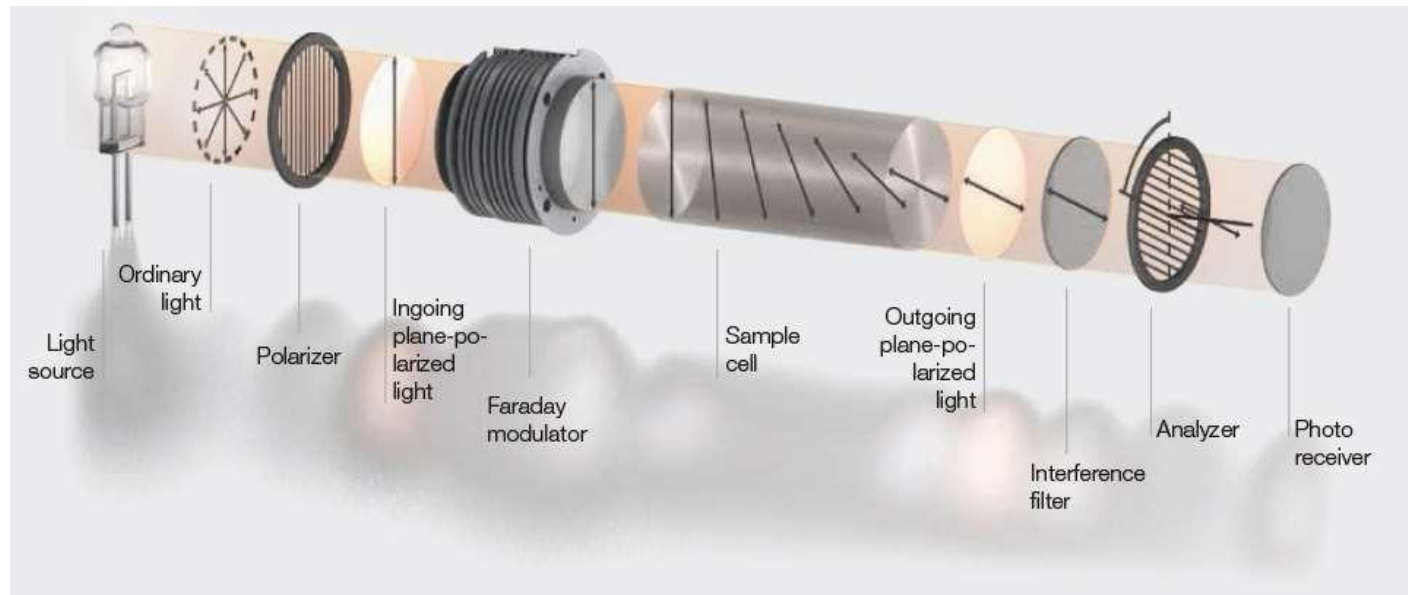
Circular Dichroism



INSTRUMENTATION

A Polarimeter consists of following parts

- Light source
- Polarizer
- Faradays modulator
- Sample cell
- Analyzer
- Detector



Schematic representation of Polarimeter

COTTON EFFECT:

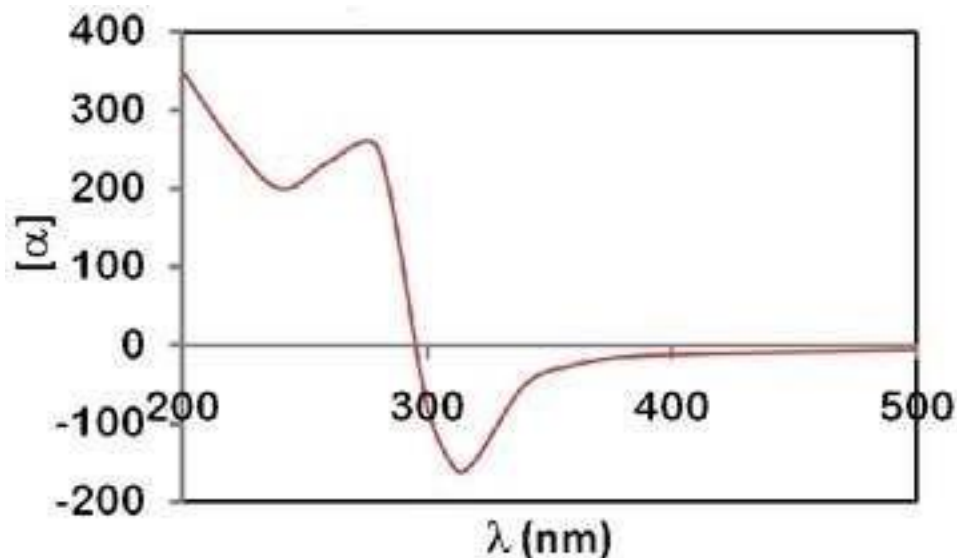
- ❖ The Cotton effect is the characteristic change in optical rotatory dispersion in the vicinity of an absorption band of a substance.
- ❖ The combination of both (circular birefringence and circular dichroism) effects in the region in which optically active absorption bands are observed gives rise to a phenomenon called **cotton effect**.
- ❖ The difference $n_L - n_R(\Delta n)$ and $e_L - e_R(\Delta e)$ vary with the wave length and can be positive or negative.

COTTON EFFECT:

- **Djerassi & Klyne** suggested that rotatory dispersion curves (i.e. plot of optical rotation against wavelength.) should be classified in to two main types.

1. Plain curves

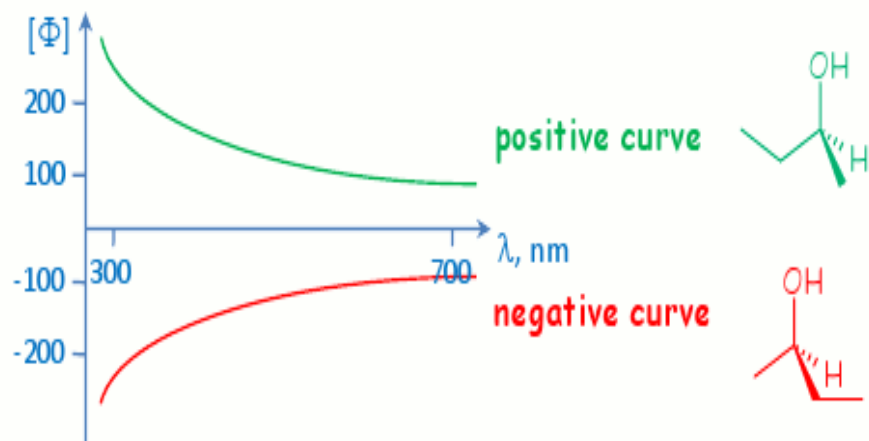
2. Cotton effect curves.



COTTON EFFECT:

Plain curves

- These are normal or plain curves.
- These curves occur at absorption maximum.
- These curves obtained for compounds which don't have any absorption in wavelength where optically active compounds are examined. Ex: Hydrocarbons, Alcohols etc



COTTON EFFECT:

Cotton effect curves

- These curves will show the high peaks & troughs which depends on the absorbing groups.
- These curves will obtain for the compounds which are having **asymmetric carbon** & **chromophore** which absorbs near UV region.
- These are again divided into 2 types, they are

1. Single cotton effect curves

2. Multiple cotton effect curves.

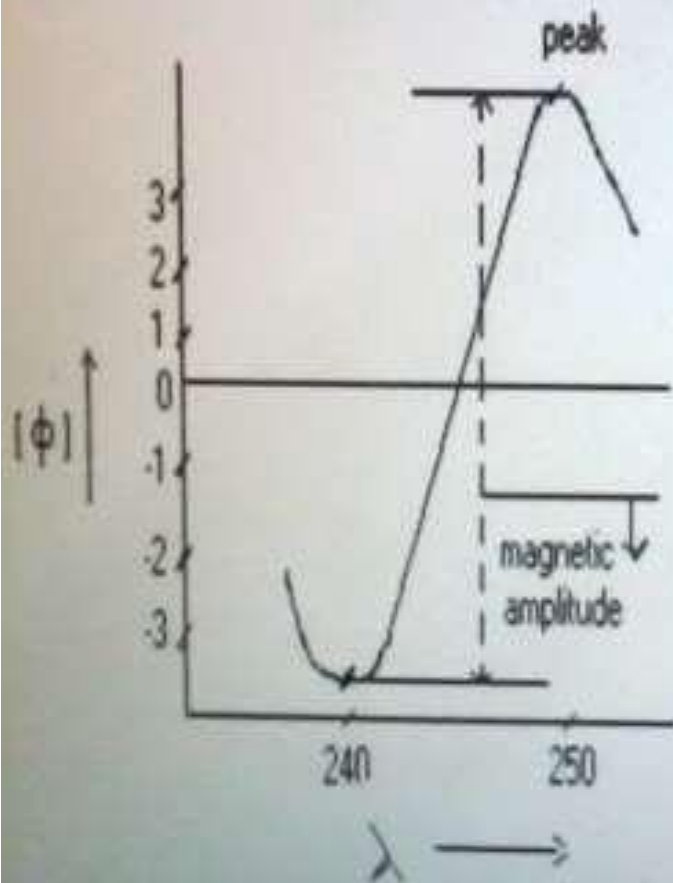
COTTON EFFECT:

Single cotton effect curves

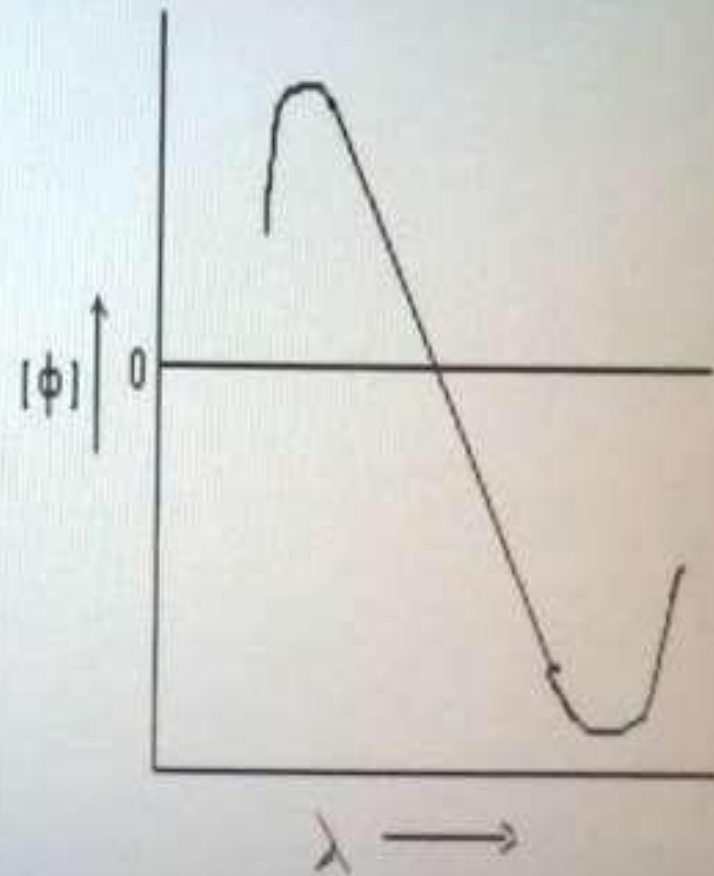
- These single cotton curves will show both maximum & minimum curves at maximum absorption.
- From the longer wavelength towards the cotton effect region if crest passes first through it then the trough it is called as **+ve cotton effect**.
- In the same manner if it happens in opposite way it is called as **-ve cotton effect**.

COTTON EFFECT:

Positive CE Curve



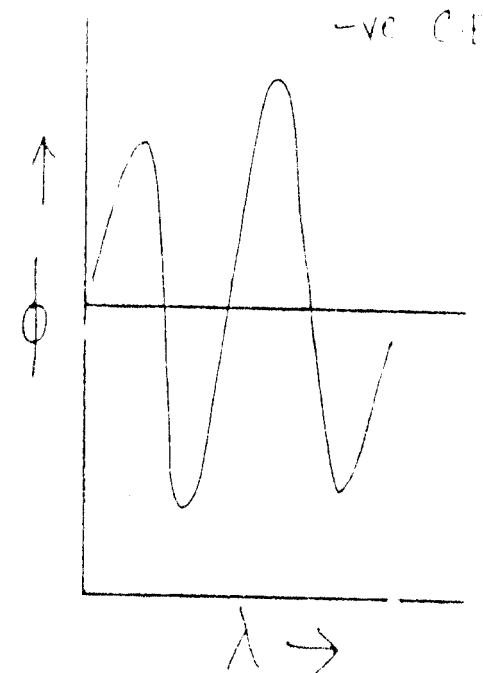
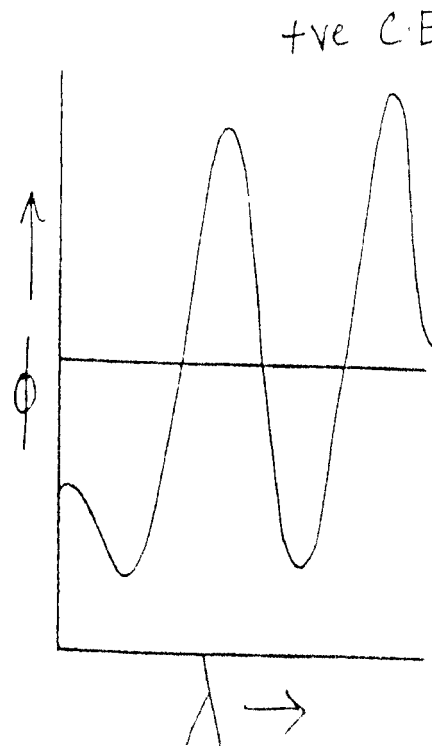
Negative CE Curve



COTTON EFFECT:

Multiple cotton effect curves

- These are a little different from the single cotton effect curves. Here more than two crests & troughs are obtained. Ex: camphor etc.



DIFFERENCES BETWEEN ORD AND CD:

OPTICAL ROTATORY DISPERSION (ORD)

ORD is If the **refractive indices** of the sample for the left and right handed polarized light are **different**, when the components are recombined, the plane polarized radiation will be rotated through an angle α

ORD spectra are **dispersive**

In ORD the circular polarized light is used is **not converted to elliptical light**

ORD graphs are obtained by plotting **specific rotation vs wavelength**

CIRCULAR DICHROISM (CD)

Circular dichroism is the **differential absorption** of left and right handed circularly polarized light

CD spectra are **absorptive**

In CD the circular polarized light is used and is **converted to elliptical light**

CD graphs are obtained by plotting molar **ellipticity vs wavelength**.

APPLICATIONS OF ORD AND CD:

- **Determination of optically active substance** such as amino acids, polypeptides, proteins, steroids, antibiotics, terpenes.
- **Stereochemistry of Aliphatic amino acids:** Aliphatic amino acids show a unique Cotton effect. α -amino acids of levo configuration show positive effect around 215nm while dextro enantiomers show negative effect.
- **Stereochemistry of Steroids:** In one form the specific rotation increases with decreasing wave length(positive curve) and in the other form the specific rotation decreases with increasing wave length(negative curve) .

SPECIFIC APPLICATIONS OF ORD:

- Quantitative Analysis: specific rotation is a good measure of concentration.
- Determination of Absolute configuration.
- Conformational studies example : (+) 3 methyl cyclohexanone.
- Equilibrium studies: If an optically active chromophore takes part in a reaction the extent of reaction can be observed by means of cotton effect.



References:

- *Organic spectroscopy* by William Kemp 3rd edition pages no 279-280.
- *Instrumental method of Chemical Analysis* by Chatwal G.R. and Anand S.K.
- *Instrumental method of Analysis* by Willard H.H., Merritt L.L., Dean J.A., Settle F.A., 6th edition.
- *Instrumental methods of Chemical Analysis* by B.K. Sharma.
- Internet