

# Optical Rotatory Dispersion (ORD)

## and Circular Dichroism (CD) - kalsi

Ordinary light  
EMV of diff.  $\lambda$

Prism  $\rightarrow$  Monochromatic light  
C light of single  $\lambda$  but vibrates in all planes

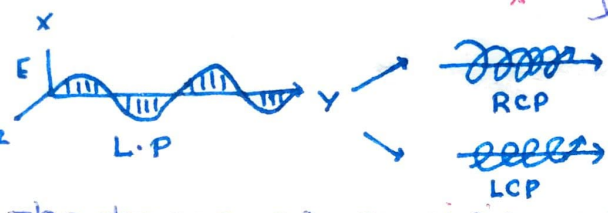
Nicol prism  $\rightarrow$  plane polarized light (single  $\lambda$  vibrates in single plane)

in ordinary electromagnetic radiation, electric field associated with the light wave oscillates in all directions perpendicular to the direction of propagation.  $\rightarrow$  but in linearly polarized light, electric field vector oscillates in one plane which contains the line along which the radiation is propagated.

$\rightarrow$  when a linearly polarized light pass through a specially cut glass prism, left and right circularly polarized light is obtained. Enantiomers rotate either clockwise or anticlockwise direction of plane polarized light

Specific rotation  $[\alpha]_{\lambda}^T = \frac{100 \times \alpha_{obs}}{lc}$

$\alpha$  = observed rotation  
 $l$  = length of polarimeter tube (in dm)  
 $c$  = conc<sup>n</sup> in g/100 cm<sup>3</sup> mL



The change of specific rotation  $[\alpha]$  or molar rotation  $[\phi]$  with wavelength of light used is called ORD (Optical rotatory dispersion).

$\rightarrow$  The differential absorption of left and right circularly polarized radiation is termed as CD. ORD, CD techniques, which differentially the two enantiomers of a chiral compd are called chiroptical techniques

### Theory

when a linearly polarized light beam passes through an optically active medium, the two circularly polarized components show different refractive indices; due to their differences in their light velocities in the medium. One will have lesser velocity than other) this phenomenon is called circular birefringence.

in plane polarized light the oscillation of particles is  $\perp$  to the direction of propagation of light particles is  $\perp$  to the direction of propagation of light particles is along the direction of propagation of light wave

Due to circular birefringence, the optically active medium will have unequal molar absorptivity coefficients for the left and right circularly polarized light. This difference in molar absorptivity is called circular dichroism (CD).

- (1) diff refractive indices ( $n_L \neq n_R$ )
- (2) diff absorption coefficients ( $k_L \neq k_R$ )

→ The combined phenomena of circular birefringence and circular dichroism are called Cotton effect.

1. Both CD and ORD are displayed by chiral compounds (not by achiral or racemic mixtures)
2. ORD involves measurement of rotation (detected over all wavelengths), CD involves measurement of absorption (detected in the vicinity of absorption band)
3.  $UV \rightarrow$  molar absorptivity versus  $\lambda$   
 $\epsilon$   
 CD  $\rightarrow$  difference in molar absorptivity ( $\Delta \epsilon$ ) or molar ellipticity versus  $\lambda$   
 $(\theta)$   
 each CD curve for each electronic absorption represents a positive or negative Cotton effect.
4. ORD curve for many compounds are the plain curve ( $+$  or  $-$ ) variance, but if some symmetric  $C=O$  chromophore is present adjacent to stereocenter, an anomalous ORD curve called Cotton effect curve is obtained.
5. Cotton effect (CE) can be either  $+$  or  $-ve$ .
6. For a CD cotton effect for a compound, there also exist corresponding ORD cotton effect.

The octant rule

→ Both UV-vis and chiroptical spectroscopy (ORD and CD) are closely related since both involve the same photophysical process, i.e. the promotion of an  $e^-$  from the ground state orbital to an excited state orbital. The difference is that UV-vis spectroscopy measures the absorption of ordinary light



associated with the promotion of an electron whereas the ORD and CD spectroscopy measures the absorption of left and right circularly polarized light and displays the difference in their absorptions

→ when a linearly polarized light beam passes through an optically active medium, its circularly polarized components show different refractive indices

[refractive index  $n$  for a medium =  $\frac{c_0}{c}$   
 $c$  = velocity of light in that medium  
 $c_0$  = velocity of light in vacuum.] due to their unequal velocities in the optically active medium.

thus the two circularly polarized components will not be in a phase, thus the resultant linear polarization vector will get rotated by an angle  $(\alpha)$  to the original plane of polarization. This change of specific rotation  $(\alpha)$  or molar rotation  $([\phi])$  with the wavelength of the light is measured in optical rotatory dispersion (ORD).

→ If the medium is achiral or a racemic mixture, the left and right circularly polarized light travel with the same velocity, thus enter and exit from the medium in same phase. Also there will be no rotation of the plane of linearly polarized light as it pass through the medium. No ORD for achiral molecules.

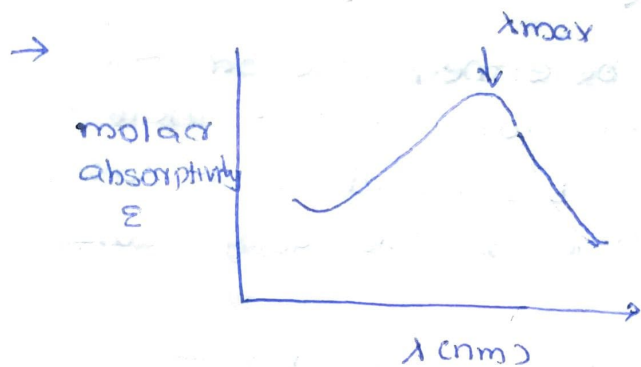
→ Due to circular birefringence (two diff refractive indices) of the optically active medium, the circularly polarized components will be absorbed to different extents; and will have unequal molar absorptivity coefficient  $(\epsilon)$  for the right and left circularly polarized light. This difference in molar absorptivity is called circular dichroism (CD).

71

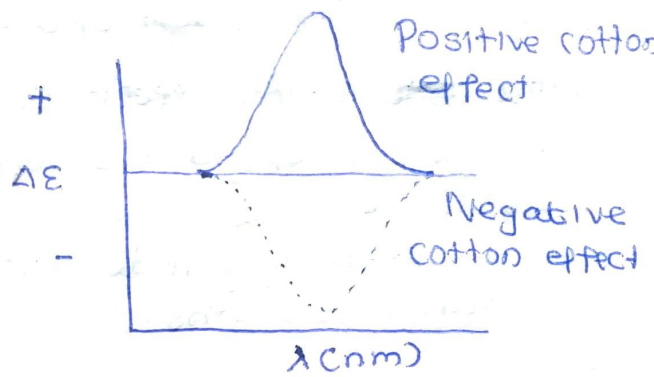
The combined phenomenon of circular birefringence and circular dichroism are called Cotton effect.

1 → chiral compds only give CD and ORD.

2 → ORD involves measurement of rotation, thus can be detected over all wave lengths. CD involves the measurement of absorption and occurs only in the vicinity of an absorption band.



UV-VIS curve

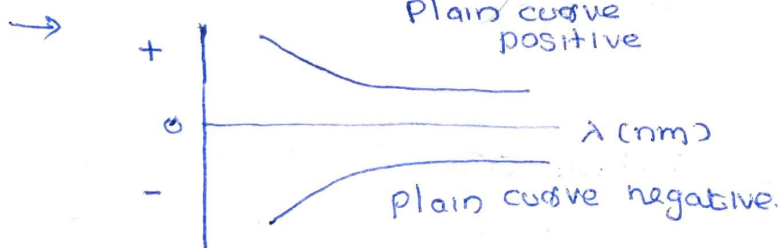


CD curve.

A CD curve has similarities with UV-VIS curve, but a CD curve can be positive or negative.

$\epsilon$  → molar absorptivity or molar extinction coefficient

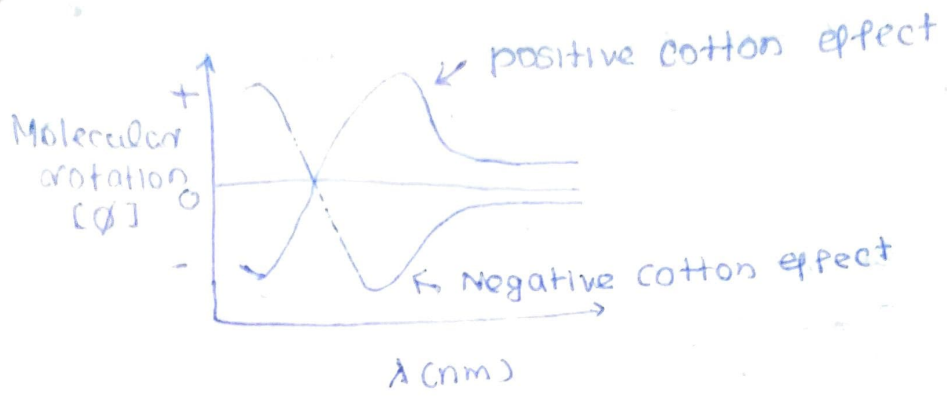
$\Delta\epsilon$  → difference in molar absorptivity.



ORD curve

The ORD curve for many compounds only show the + or - plane curves as shown above. However if the compound with a symmetric chromophore ( $C=O$  group) has an adjacent asymmetric unit (stereocentre) an anomalous ORD curve called a Cotton effect curve is obtained. Thus the ORD curve of an optically active ketone in the region of  $n \rightarrow \pi^*$  transition band ( $\sim 290$  nm), one will observe the Cotton effect.

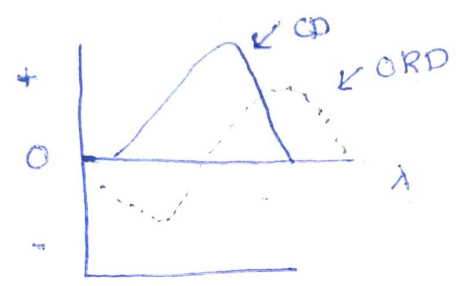




Anomalous ORD curve

→ The ~~Cott~~ Cotton effect could be either +ve or -ve. The curve is called +ve when the rotation first increases with the decreased wavelengths and it is termed as -ve when the rotation magnitude first decreases when going towards shorter wave lengths.

→ For a CD Cotton effect (at a given wavelength) for a compound, there also exist a corresponding ORD Cotton Effect.



Cotton effect

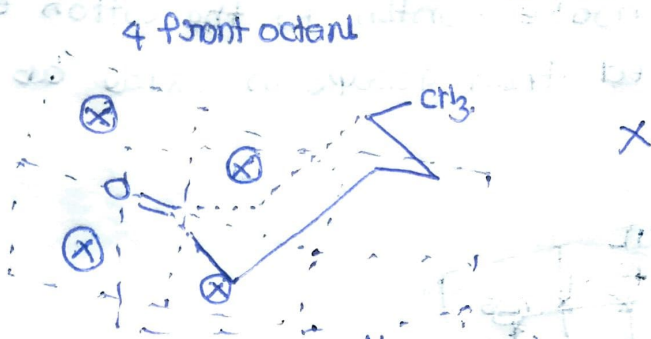
Any medium which is exhibiting circular birefringence may also exhibit circular dichroism. The combination of these two effects in the region in which the optically active absorption bands are observed give rise to the phenomenon called cotton effect

Octant rule

The sign of cotton effect reflects the stereo chemistry of the environment of the chromophore. eg: of a chiral ketone. Octant rule is used to predict the sign of the cotton effect in ORD and CD curves from the knowledge of the spatial arrangement (axial or equatorial) of the substituents around the carbonyl

group. This rule has been used to predict the absolute configuration of compounds of unknown stereostructure.

→ considers the cyclohexanone ring in the chair conformation having an equatorial methyl group.



1. The ring containing the carbonyl group is oriented such that it occupies the head of the chair closest to the observer.

2. Three planes at right angles are drawn through the carbonyl group to produce eight octants

3. Front octants are usually vacant, so in octant rule only rear octants are considered.

→ First plane (A) passes through carbonyl group C-1 and C-4.

→ Second horizontal plane (B) is put through C-1 and the cyclohexanone is so tilted that it also passes through C-2 and C-6.

→ Third plane (C) passes about midway through the C=O bond at right angles.

4. The overall sign of the  $n \rightarrow \pi^*$  Cotton effect is then determined by the contributions of the groups in these octants

5. According to octant rule

(a) The substituents lying on the coordinate planes make negligible contribution to the  $n \rightarrow \pi^*$  Cotton effect.

Equatorial substituent at C-2 and C-6 (Plane B)

- No contrib.

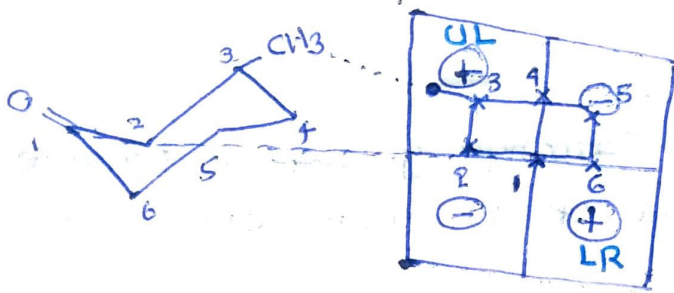
at C-4

Axial and equatorial substituents (Plane A) - No contrib.



Axial C-2 + all subst at C-5  $\rightarrow$  <sup>+ve</sup> Positive<sup>ve</sup> Contribn 79  
 Axial C-6 + all subs at C-3  $\rightarrow$  <sup>-ve</sup> Negative<sup>ve</sup> Contribn.

6. Substituents which are far removed from the carbonyl group at C-3 or C-5 make contribn to the cotton effect however are less marked than groups in axial at C-2 and C-6.

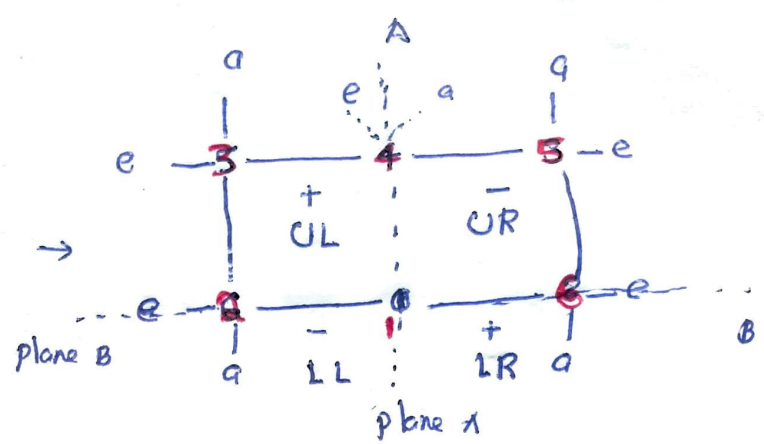
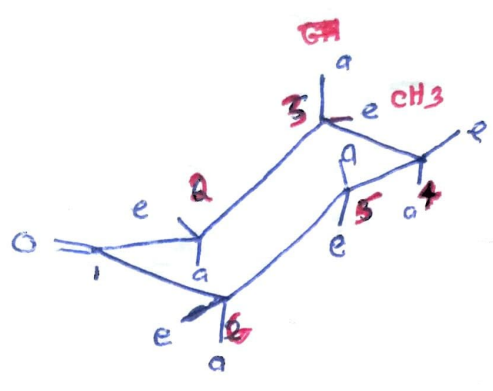


equatorial  
 3-Methyl cyclohexanone will show a positive cotton effect

\* See page NO 137 for applications and details.

5(b) - Substituents lying in the (+) sectors (UL and LR) make a positive contribution and substituents lying in the (-) sectors (UR and LL) make a negative contribution to the cotton effect. Thus the groups in upper left quadrant and axial groups in the lower right contribute to a positive cotton effect, and the groups in the upper right and the axial substituents in the lower left contribute to a negative cotton effect. The operation of the octant rule can be summarized as follows

Axial and equatorial groups +ve cotton effect	Axial and equatorial groups -ve cotton effect
Axial groups only -ve cotton effect	Axial groups only +ve cotton effect



Result Octants  
(Front view)