UNIT 4: ORD and CD

(Part III: Cotton effect, Faraday and Kerr effects)

M.Sc. Semester II

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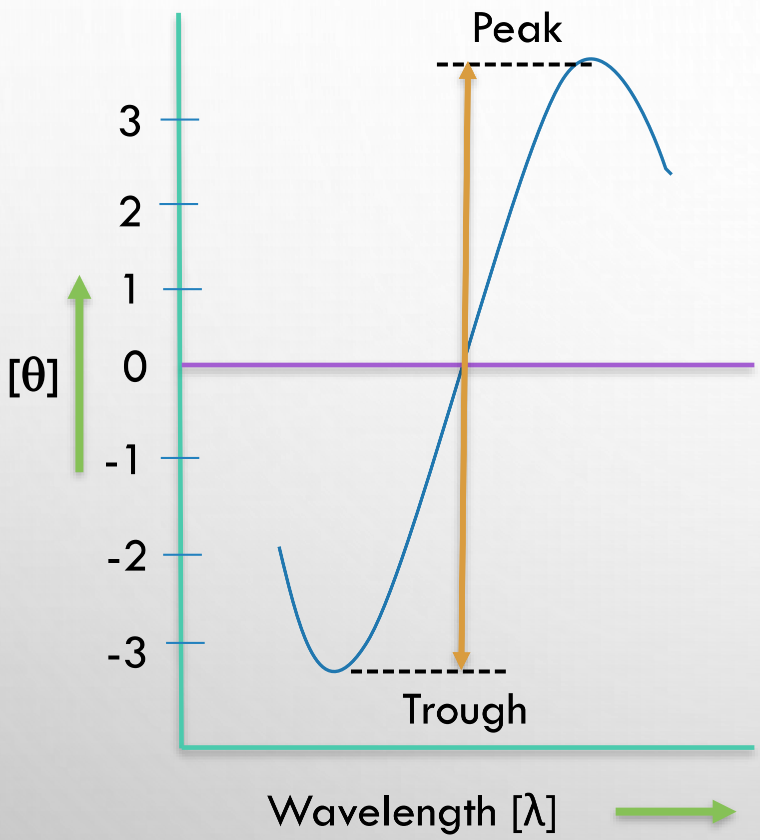
COTTON EFFECT

- In the late nineteenth century, Cotton studied optical rotatory dispersion curves of compounds in the region of their absorptions, where both optical rotation and circular dichroism occur simultaneously.
- He noticed that not only is it possible to observe the circular dichroism and ellipticity in an absorption region, but also that the shape of optical rotatory dispersion (ORD) curves inside the absorption region differs markedly from their shape outside these regions.
- For many years ORD curves inside absorption regions were referred to as "anomalous" ORD curves, but this is erroneous, since this shape is the usual one for ORD curves inside these regions.
- *The combination of the appearance of circular dichroism (and ellipticity) and an S-shaped ORD curve for an optically active compound inside its absorption region is known as the* ***Cotton Effect****.*

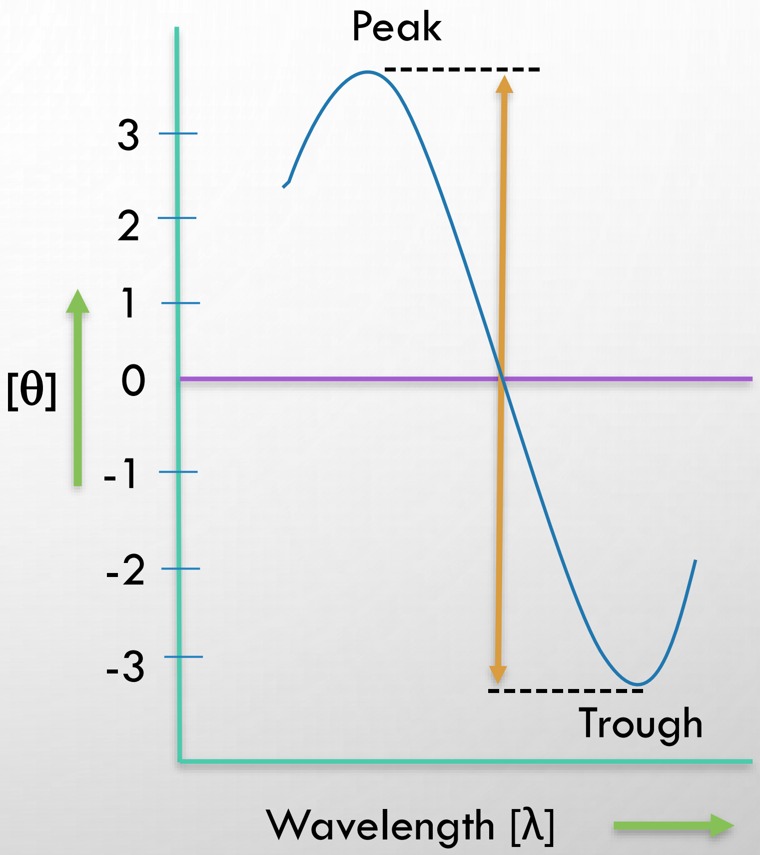
Cotton Effect Curves

- In a wavelength region where the light is absorbed, absolute magnitude of the optical rotation at first varies rapidly with wavelength, crosses zero at absorption maxima and then again varies rapidly with wavelength but in opposite direction.
- The each Cotton effect consists of two extremes, a geometric maximum called a "peak" and a geometric minimum called a "trough".
- The Cotton effect is called positive if the optical rotation first increases as the wavelength decreases that means positive Cotton effect curve has its peak in the longer wavelength region, while it is called negative if optical rotation first decreases as the wavelength decreases.
- Negative Cotton effect curve is defined as having its trough appearing at the longer wavelength.
- Optically pure enantiomers always display opposite Cotton effect ORD curves of identical magnitude.

Cotton Effect Curves



Positive cotton Effect Curve



Negative cotton Effect Curve

Cotton Effect Curves

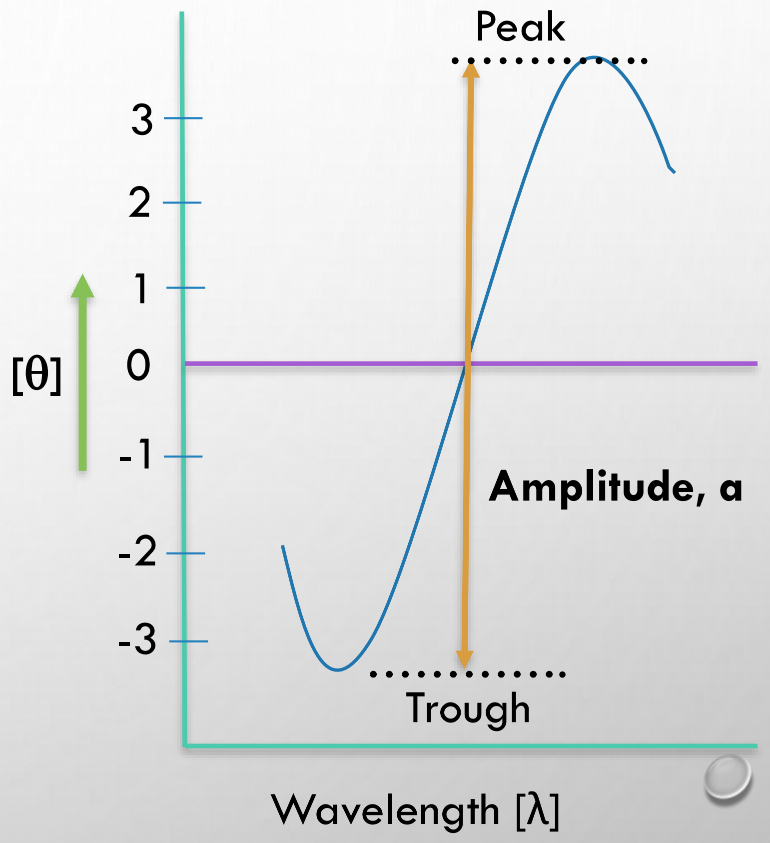
- Cotton effect curves are obtained for optically active compounds having chromophores absorbing in the near UV region.
- They show peaks and troughs depending on the absorbing groups present in the system and thus these are called an anomalous dispersion of optical rotation. These are again divided into two categories;
- (i) Single Cotton effect curves
- (ii) Multiple Cotton effect curves

Single Cotton effect curves

- These are anomalous dispersion curves which show maximum and minimum both occurring in the region of maximum absorption. So there appears only one peak and one trough in the Single Cotton effect curves. The vertical distance between peak and trough is called amplitude “a”. Amplitude is measured in degrees.

Molecular amplitude, $a = \frac{\theta_1 - \theta_2}{100}$

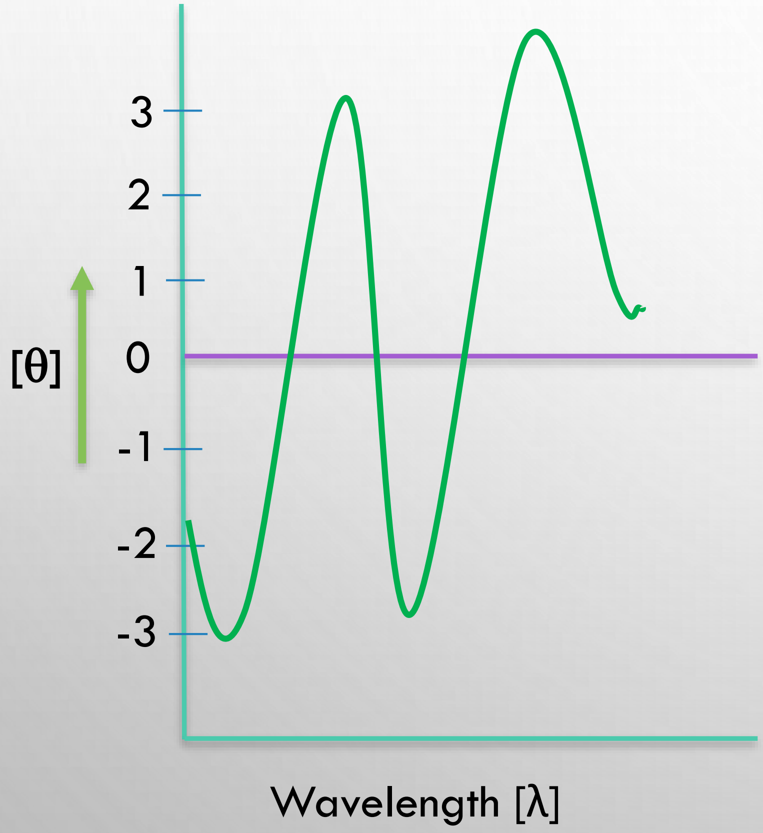
Where θ_1 is molar rotation of trough or peak from shorter wavelength and θ_2 is the molar rotation of extreme peak or trough from higher wavelength.



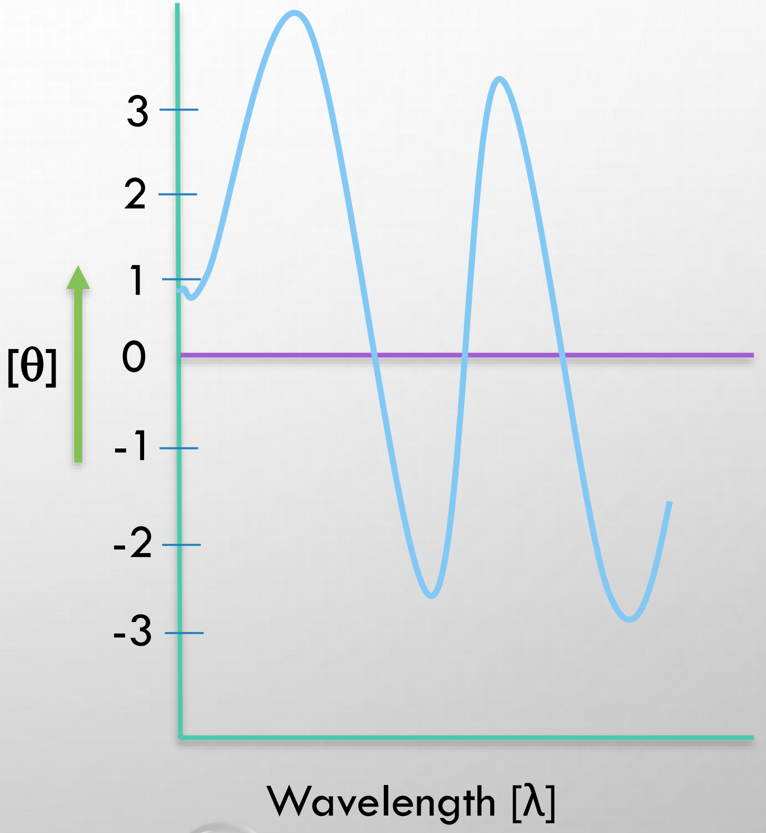
Single cotton Effect Curve

Multiple Cotton effect curves

- These are a little different from the single Cotton effect curves. They contain more than one peak and one trough.



Positive Multiple CE Curve



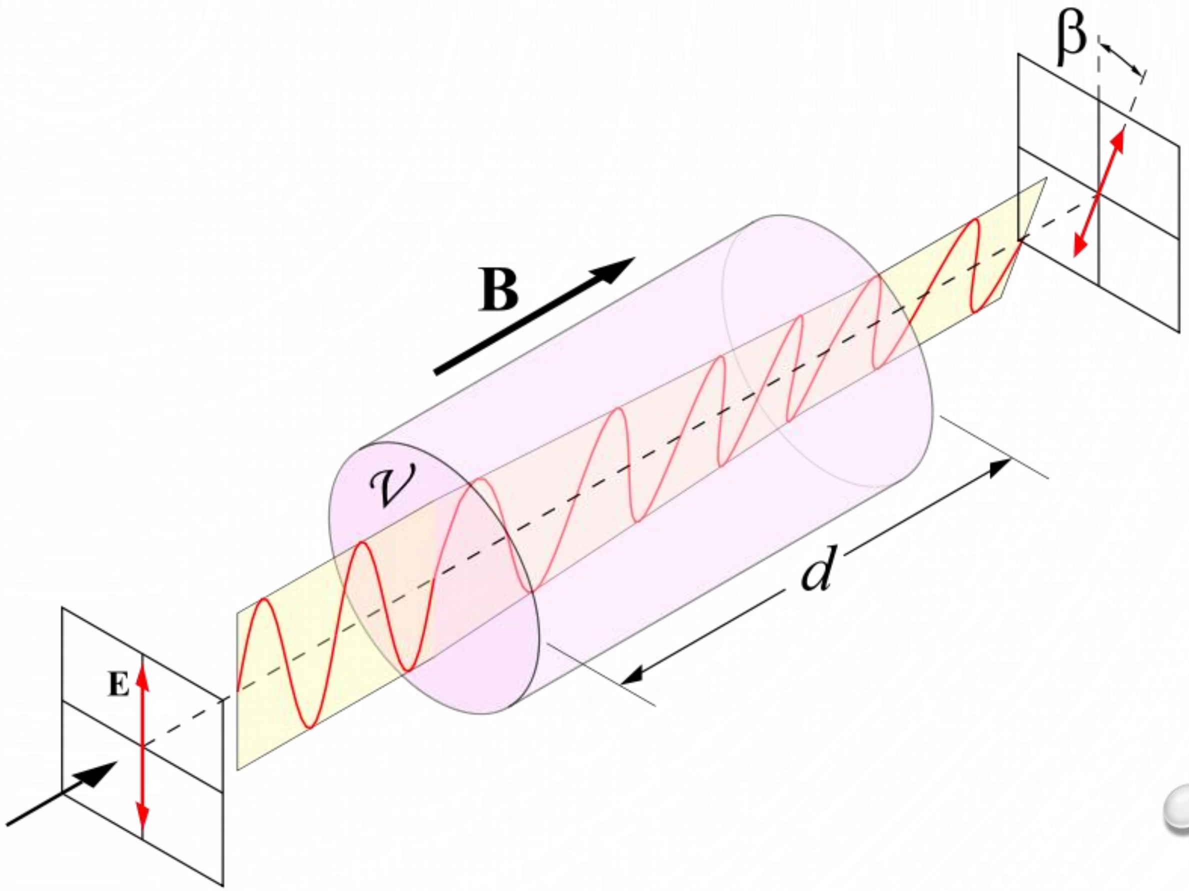
Negative Multiple CE Curve

Faraday Effect

- An interaction between light and a magnetic field in a medium. The Faraday effect causes a rotation of the plane of polarization which is linearly proportional to the component of the magnetic field in the direction of propagation.
- In circularly polarized light the direction of the electric field rotates at the frequency of the light, either clockwise or counter-clockwise. In a material, this electric field causes a force on the charged particles comprising the material (because of their low mass, the electrons are most heavily affected).
- The motion thus effected will be circular, and circularly moving charges will create their own (magnetic) field in addition to the external magnetic field.
- There will thus be two different cases: the created field will be parallel to the external field for one (circular) polarization, and in the opposing direction for the other polarization direction – thus the net B field is enhanced in one direction and diminished in the opposite direction.

Faraday Effect

The change in the dynamics of the interaction for each beam and one of the beams will be slowed down more than the other, causing a phase difference between the left- and right-polarized beam. When the two beams are added after this phase shift, the result is again a linearly polarized beam, but with a rotation in the polarization direction.



Picture credit: https://commons.wikimedia.org/w/index.php?curid=1945979

Faraday Effect

The relation between the angle of rotation of the polarization and the magnetic field in a transparent material is:

$\beta = \nu B d$

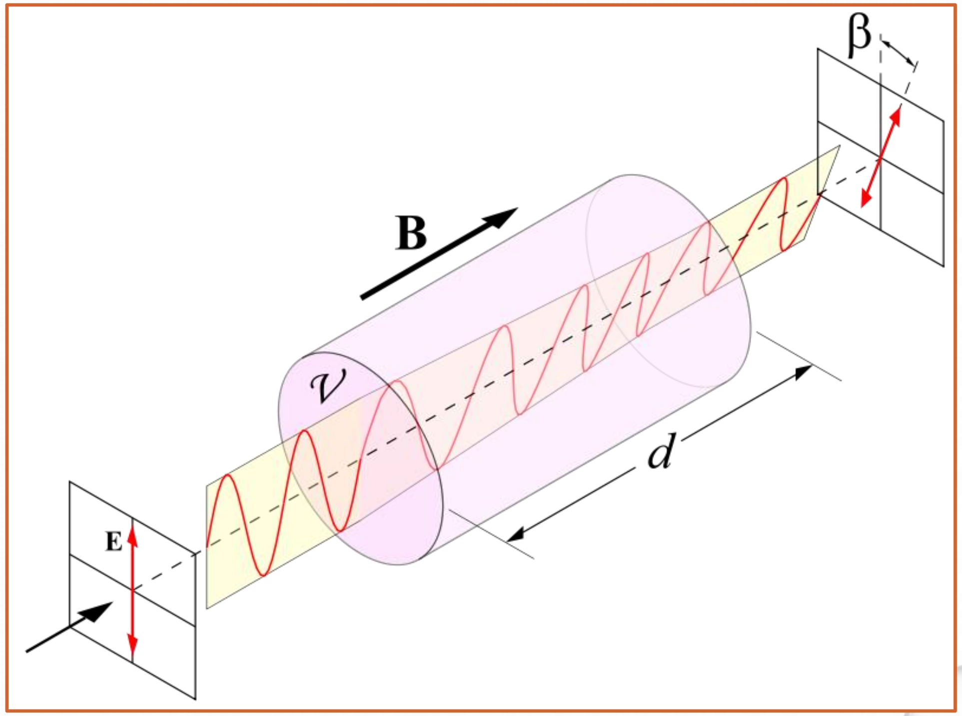
where,

β is the angle of rotation (in radians)

B is the magnetic flux density in the direction of propagation (in teslas)

d is the length of the path (in meters) where the light and magnetic field interact

ν is the Verdet constant for the material. This empirical proportionality constant (in units of radians per tesla per meter) varies with wavelength and temperature.



Kerr Effect

The Kerr effect is a change in the refractive index of a material in response to an applied electric field.

It is the special case in which a slowly varying external electric field is applied by, for instance, a voltage on electrodes across the sample material. Under this influence, the sample becomes birefringent, with different indices of refraction for light polarized parallel to or perpendicular to the applied field. The difference in *index of refraction*, Δn, is given by

$$\Delta n = \lambda K E^2$$

where λ is the wavelength of the light, K is the Kerr constant, and E is the strength of the electric field. This difference in index of refraction causes the material to act like a waveplate when light is incident on it in a direction perpendicular to the electric field.

References

- Module 25: Spectroscopic methods for determination of Absolute Configuration of Coordination Complexes, e-pathshala.
- Wikipedia

THANK YOU

Next.....

Part IV: Application of ORD & CD in determining absolute configuration of metal complexes.