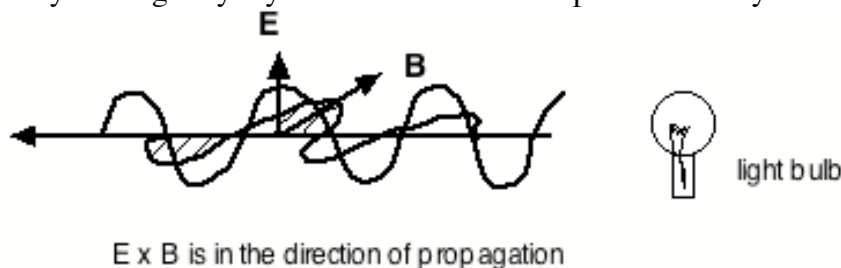


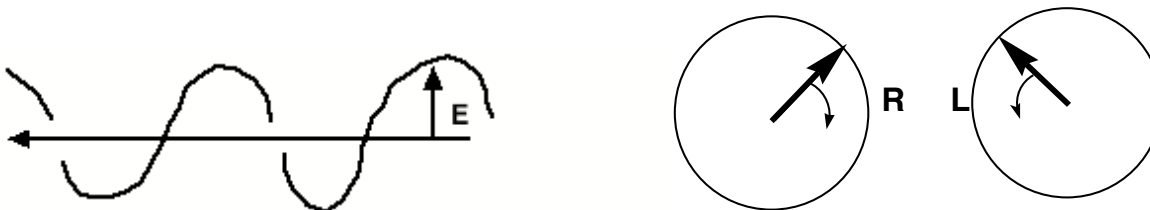
**DEMO of optical activity**

Processes involving chiral molecules are often most easily monitored by following a process known as "optical activity". Enantiomeric molecules have the same properties, unless they are in a chiral environment. One way in which this can occur is by illuminating samples of chiral molecules with "chiral light"; the two different mirror image molecules will interact with the chiral light source differently; for example, their absorption spectra will be different.

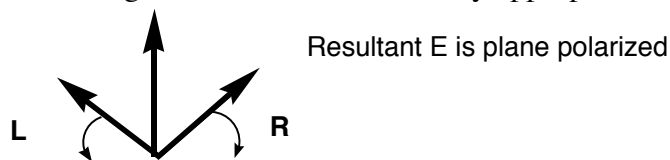
Light has associated both electric and magnetic fields. It is possible to prepare plane-polarized light by passing unpolarized light through a highly anisotropic material, such as Polaroid filters, which absorb all light with the electric field pointing in one direction (say horizontal), thereby leaving only rays whose electric fields point vertically:



It is also possible to generate circularly polarized radiation where the E field rotates around the direction of propagation. If the rotation is clockwise as one views the oncoming beam, the light is right circularly-polarized and if the rotation is counter-clockwise it is left circularly-polarized:



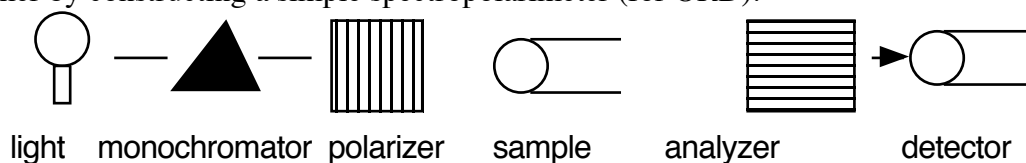
Plane and circularly polarized light can be interconverted by appropriate combinations:



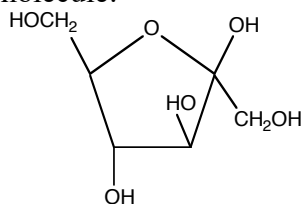
## Ch1b optical activity demo

Now, the significance of this is that circularly polarized light exists in two forms that are either right or left handed. Chiral molecules will interact differently with right and left circularly polarized light, and this property can be used to characterize enantiomeric species.

Experimentally, this can be measured in two ways - by looking at rotation of plane polarized light (optical rotatory dispersion) due to differences in the refractive indices for R and L circularly polarized light, or by looking at absorption of circularly polarized light (circular dichroism) due to differences in extinction coefficients for R and L. Our demo will use the former by constructing a simple spectropolarimeter (for ORD):

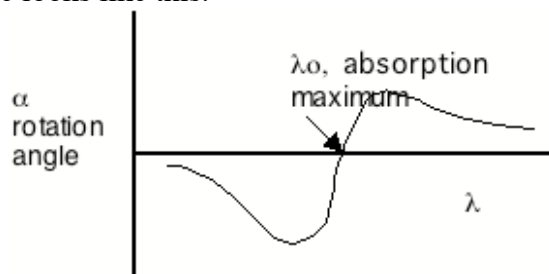


CORN SYRUP provides an example of a compound (fructose) with intrinsic optical activity, meaning there is no mirror plane in molecule:



The color of the transmitted light varies with rotation angle. Why?

Ideally, one would measure rotation angle  $\alpha$  as a function of monochromatic wavelength  $\lambda$ . A typical plot curve looks like this:

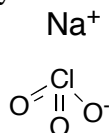


## Ch1b optical activity demo

For  $\lambda > \lambda_0$ , the rotation angle decreases further away from the absorption peak. So, for sugars with  $\lambda_0$  in the UV, blue light is transmitted at small rotation angles since red is absorbed, while at larger angles, red/yellow is seen since blue is absorbed.

As in this example (corn syrup), chirality in the early days was associated with life, since chemists could never make just one enantiomer: Pasteur in Fruton: *Molecules & Life* pg. 53 Pasteur, 1860 “The artificial products do not have any molecular dissymetry (ie - they are not chiral (achiral)), and I could not indicate the existence of a more profound separation between the products born under the influence of life and all others.” But, can also see chirality in abiotic systems:

SODIUM CHLORATE crystals - example of system where achiral molecule is placed in chiral environment - this is a second mechanism by which optical activity can be generated:



In  $\text{NaClO}_3$ , all the O-Cl-O bond angles are  $106.7^\circ$  (pyramidal structure). As the chlorate anion has mirror planes, solutions of this salt are achiral (non-optically active). However, crystals of sodium chlorate are chiral due to formation of helical arrays in the lattice with either right or left handed twist. These can be seen between cross-polarizers, as crystals will either rotate the plane of polarization towards the right or towards the left. In any one crystal, there is a 50:50 chance of getting a given hand. Can resolve two hands manually, just like Pasteur; but, upon dissolution, the solution will no longer rotate light. Expect equal amounts of two hands of crystals, but can get spontaneous chirality, depending on stirring rate – see *Science* **250**, 975 (1990) and *J. Chem. Ed.* **69**, 468 (1992). Crystallization in the presence of chiral compounds can also lead to unequal amounts of the two hands (Kipping & Pope, *JCS Trans.* **73**, 606 (1898)). V. Schomaker in the spring of 1997 noted after J. Dunitz’s seminar that this phenomenon of spontaneous chirality was first discovered over 100 years ago, as described in Grote (?).