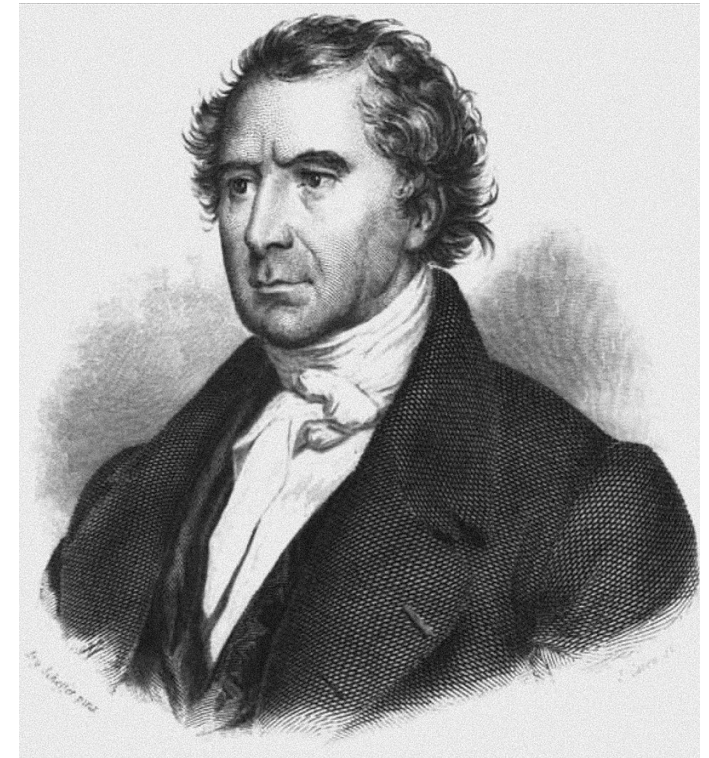


Actividad óptica

Actividad óptica

- La manera en la que la luz interactúa con una sustancia material puede proveer información sobre su estructura molecular.
- En 1811 Dominique (François) Arago observa la rotación continua de la dirección de polarización lineal al **propagarse la luz sobre el eje óptico del cuarzo**



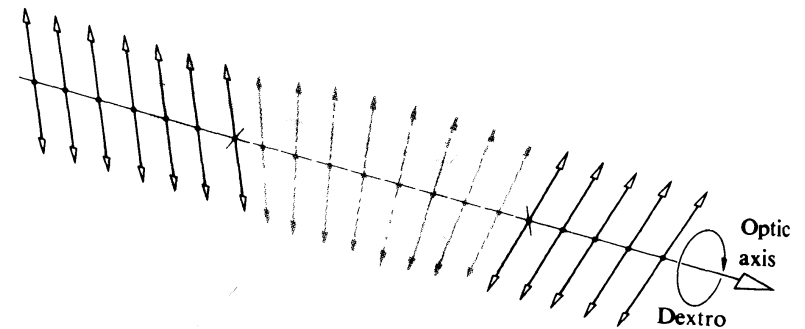
Dominique François Jean Arago

Actividad óptica

- Todo material que genera una rotación del campo \vec{E} de una onda lineal plana que lo atraviesa se denomina **ópticamente activo**.
- Al mismo tiempo que Arago, Jean Baptiste Biot diferencia rotaciones:
 - **Dextrógiras** (sentido horario mirando a la fuente)
 - **Levógiras** (antihorario)
- Distintos sentidos corresponden a distintas estructuras cristalinas.



Jean Baptiste Biot



rotación dextrógira del cuarzo

Explicación fenomenológica de Fresnel

- Planteó que la actividad óptica corresponde a distintos índices de refracción para distintos sentidos de polarización circular (Birrefringencia circular)



Augustin-Jean Fresnel

Flashback

- ¿Qué polarización resulta de sumar dos ondas circularmente polarizadas de igual amplitud y sentido opuesto?

$$\vec{\mathbf{E}}_{\mathcal{R}} = E_0[\hat{\mathbf{i}} \cos(kz - \omega t) + \hat{\mathbf{j}} \sin(kz - \omega t)]$$

Polarización derecha (horaria)

$$\vec{\mathbf{E}}_{\mathcal{L}} = E_0[\hat{\mathbf{i}} \cos(kz - \omega t) - \hat{\mathbf{j}} \sin(kz - \omega t)]$$

Polarización izquierda (antihorario)

Explicación fenomenológica de Fresnel

- Planteó que la actividad óptica corresponde a distintos índices de refracción para distintos sentidos de polarización circular (Birrefringencia circular)
- Como la polarización lineal es la suma de dos ondas polarizadas circularmente en sentidos opuestos, al entrar en una sustancia ópticamente activa se produce una diferencia de fase entre las ondas polarizadas circularmente lo cual da como resultado una rotación en la dirección de polarización.



Augustin-Jean Fresnel

Explicación fenomenológica de Fresnel

- Supongamos dos ondas **de la misma frecuencia y amplitud** polarizadas circularmente en sentidos opuestos:

$$\vec{\mathbf{E}}_{\mathcal{R}} = \frac{E_0}{2} [\hat{\mathbf{i}} \cos (k_{\mathcal{R}}z - \omega t) + \hat{\mathbf{j}} \sin (k_{\mathcal{R}}z - \omega t)] \quad \text{Polarización derecha}$$

$$\vec{\mathbf{E}}_{\mathcal{L}} = \frac{E_0}{2} [\hat{\mathbf{i}} \cos (k_{\mathcal{L}}z - \omega t) - \hat{\mathbf{j}} \sin (k_{\mathcal{L}}z - \omega t)] \quad \text{Polarización izquierda}$$

- Como la frecuencia es la misma, la relación entre k y n queda

$$k_{\mathcal{R}} = k_0 n_{\mathcal{R}} \quad \text{y} \quad k_{\mathcal{L}} = k_0 n_{\mathcal{L}}.$$

Explicación fenomenológica de Fresnel

- El campo resultante de la suma de ambas ondas es:

$$\vec{\mathbf{E}} = \vec{\mathbf{E}}_{\mathcal{R}} + \vec{\mathbf{E}}_{\mathcal{L}},$$

- Donde

$$\vec{\mathbf{E}}_{\mathcal{R}} = \frac{E_0}{2} [\hat{\mathbf{i}} \cos (k_{\mathcal{R}}z - \omega t) + \hat{\mathbf{j}} \sin (k_{\mathcal{R}}z - \omega t)]$$

$$\vec{\mathbf{E}}_{\mathcal{L}} = \frac{E_0}{2} [\hat{\mathbf{i}} \cos (k_{\mathcal{L}}z - \omega t) - \hat{\mathbf{j}} \sin (k_{\mathcal{L}}z - \omega t)]$$

Explicación fenomenológica de Fresnel

- Consideremos las igualdades trigonométricas siguientes:

$$\cos \theta + \cos \varphi = 2 \cos \left(\frac{\theta + \varphi}{2} \right) \cos \left(\frac{\theta - \varphi}{2} \right)$$

$$\sin \theta - \sin \varphi = 2 \cos \left(\frac{\theta + \varphi}{2} \right) \sin \left(\frac{\theta - \varphi}{2} \right)$$

Explicación fenomenológica de Fresnel

- Tomando $\theta = k_R z - \omega t$ y $\varphi = k_L z - \omega t$ tenemos:

$$\frac{\theta + \varphi}{2} = \frac{k_R + k_L}{2} z - \omega t$$

y

$$\frac{\theta - \varphi}{2} = \frac{k_R - k_L}{2} z$$

Explicación fenomenológica de Fresnel

- Entonces, sumando las componentes x e y por separado y sacando factor común

$$E_0 \cos [(k_{\mathcal{R}} + k_{\mathcal{L}})z/2 - \omega t] \quad \text{tenemos:}$$

$$\begin{aligned} \vec{\mathbf{E}} = E_0 \cos [(k_{\mathcal{R}} + k_{\mathcal{L}})z/2 - \omega t] & [\hat{\mathbf{i}} \cos (k_{\mathcal{R}} - k_{\mathcal{L}})z/2 \\ & + \hat{\mathbf{j}} \sin (k_{\mathcal{R}} - k_{\mathcal{L}})z/2] \end{aligned} \quad (8.36)$$

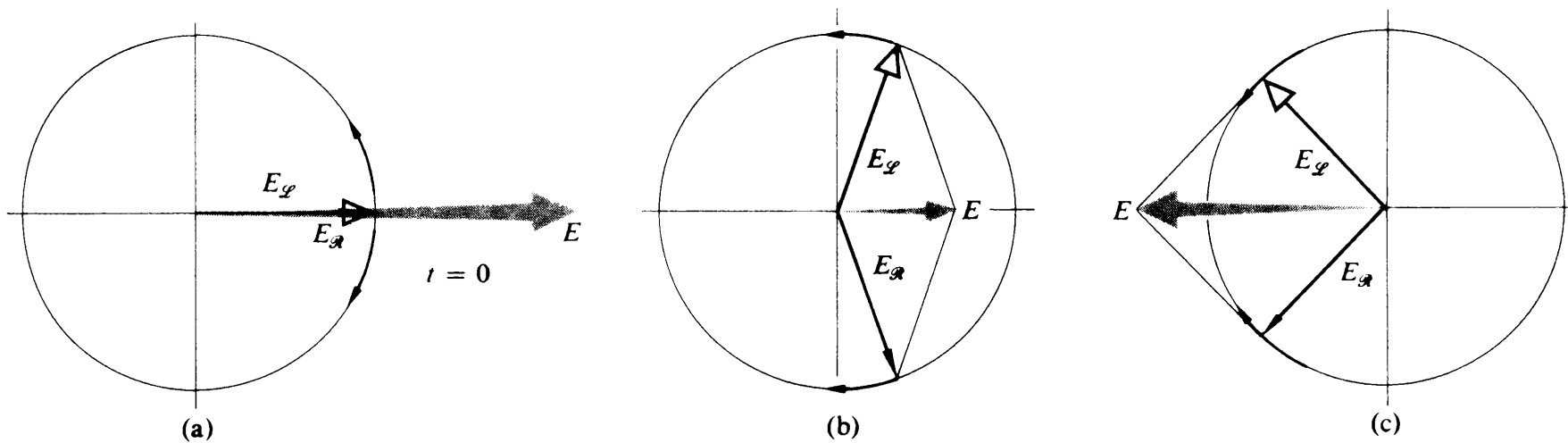
- Esto quiere decir que la oscilación se da en la dirección del vector:

$$\hat{\mathbf{i}} \cos \left(\frac{k_{\mathcal{R}} - k_{\mathcal{L}}}{2} z \right) + \hat{\mathbf{j}} \sin \left(\frac{k_{\mathcal{R}} - k_{\mathcal{L}}}{2} z \right)$$

Explicación fenomenológica de Fresnel

- Si tomamos $z = 0$ como el punto de entrada en el material, ahí tenemos que:

$$\vec{E} = E_0 \hat{i} \cos \omega t$$

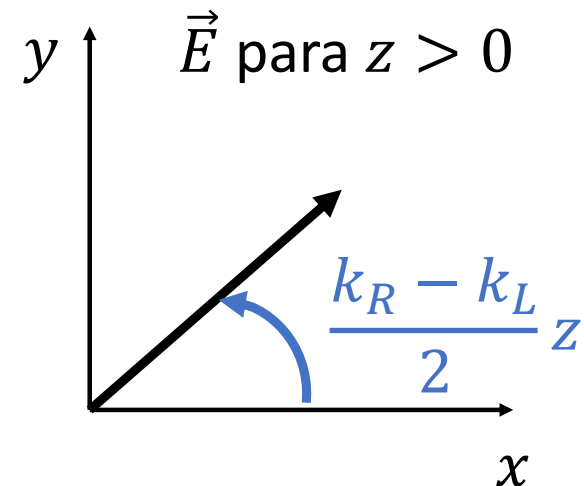


Explicación fenomenológica de Fresnel

- Como la oscilación de \vec{E} dentro del material ocurre en la dirección del vector:

$$\hat{i} \cos\left(\frac{k_R - k_L}{2} z\right) + \hat{j} \sin\left(\frac{k_R - k_L}{2} z\right)$$

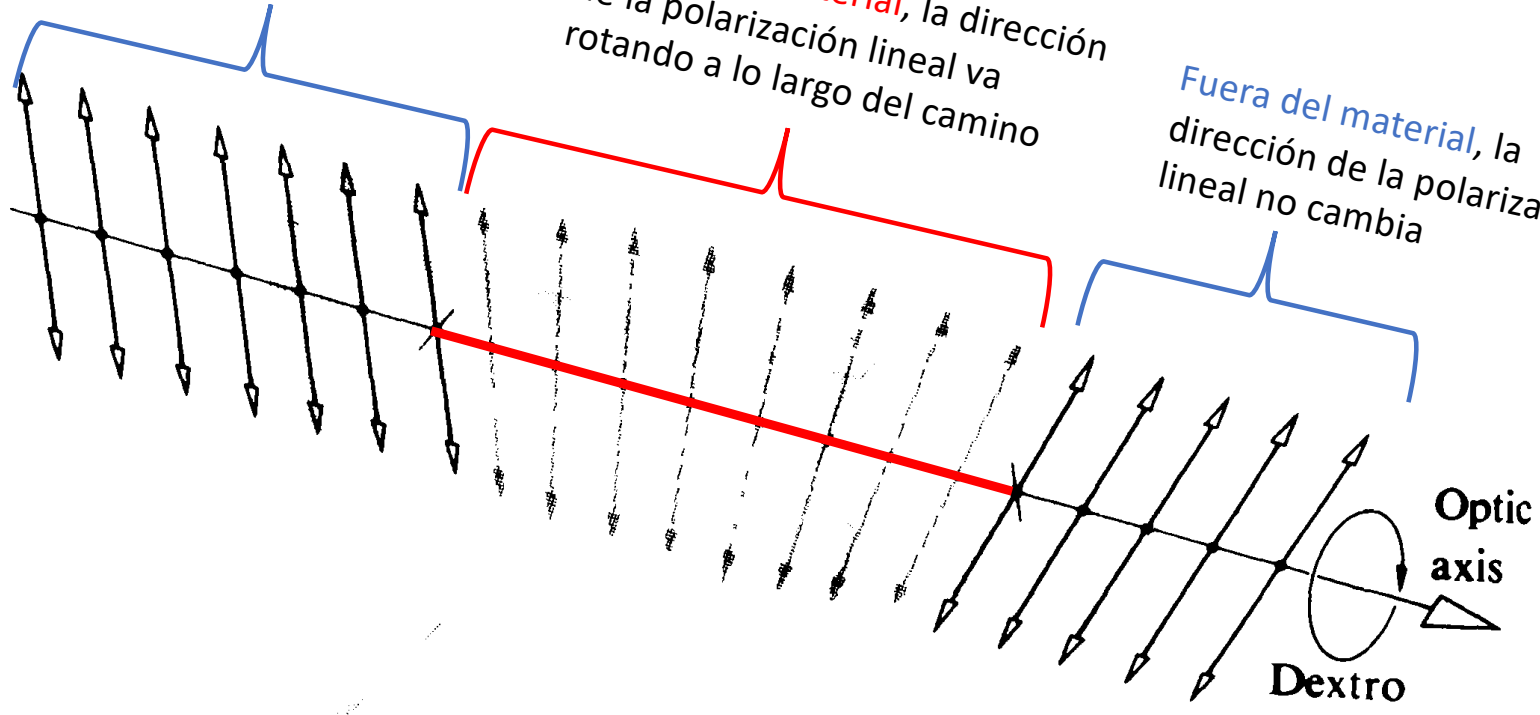
- La dirección de la polarización lineal depende de z y de k_R y k_L .
- Para $k_R > k_L$ rotación antihoraria.
- Para $k_R < k_L$ rotación horaria.



Fuera del material, la dirección de la polarización lineal no cambia

Dentro del material, la dirección de la polarización lineal va rotando a lo largo del camino

Fuera del material, la dirección de la polarización lineal no cambia



Explicación fenomenológica de Fresnel

- Tradicionalmente, el ángulo β de rotación de \vec{E} dentro del material se define **positivo cuando es horario, y negativo cuando es antihorario**.
- Entonces β se define como:

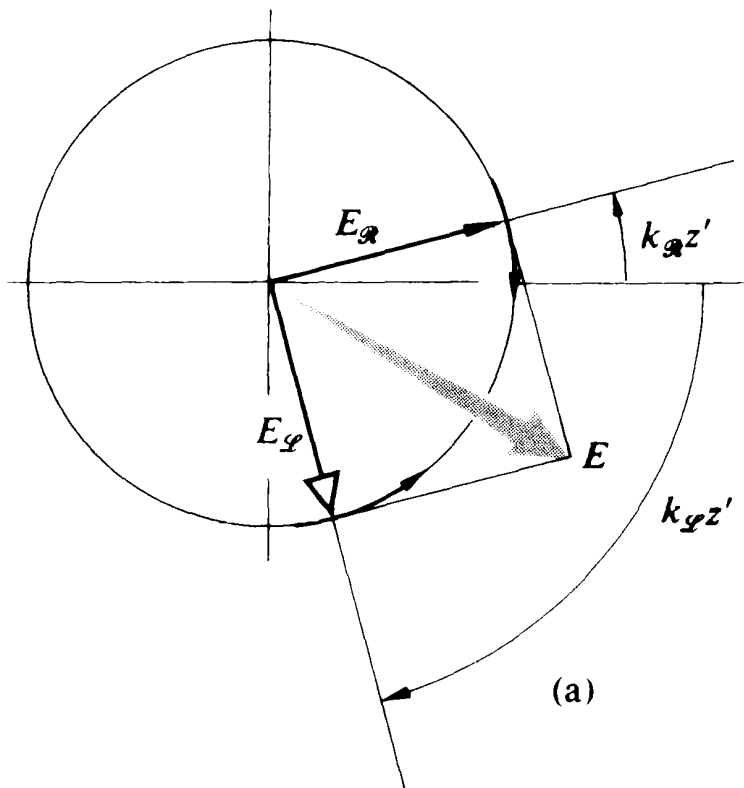
$$\beta(z) = -\frac{k_R - k_L}{2} z$$

- Si el medio tiene un espesor d , el ángulo de rotación β respecto a la entrada es:

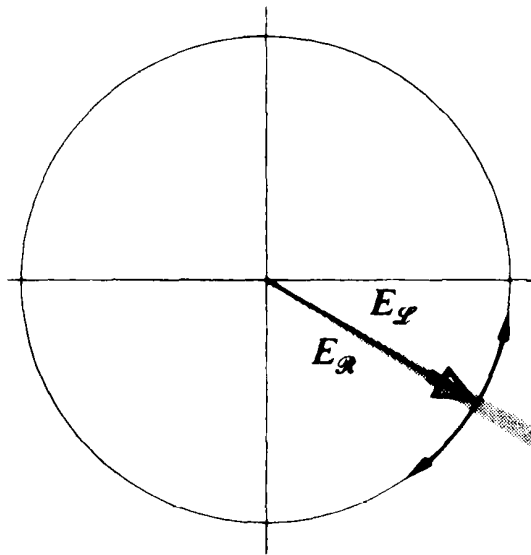
$$\beta(d) = \frac{n_L - n_R}{\lambda} \pi d$$



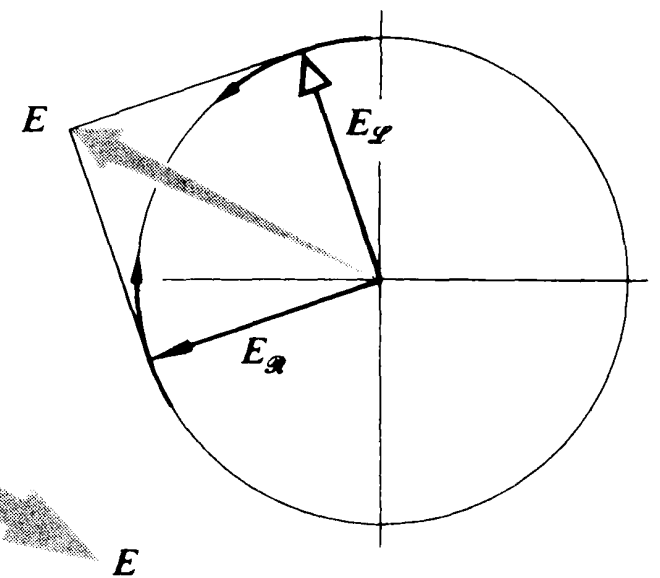
Oscilación de \vec{E} para $z > 0$ y $k_L > k_R$ (dextrógiro)



(a)



(b)



(c)

Poder rotatorio específico

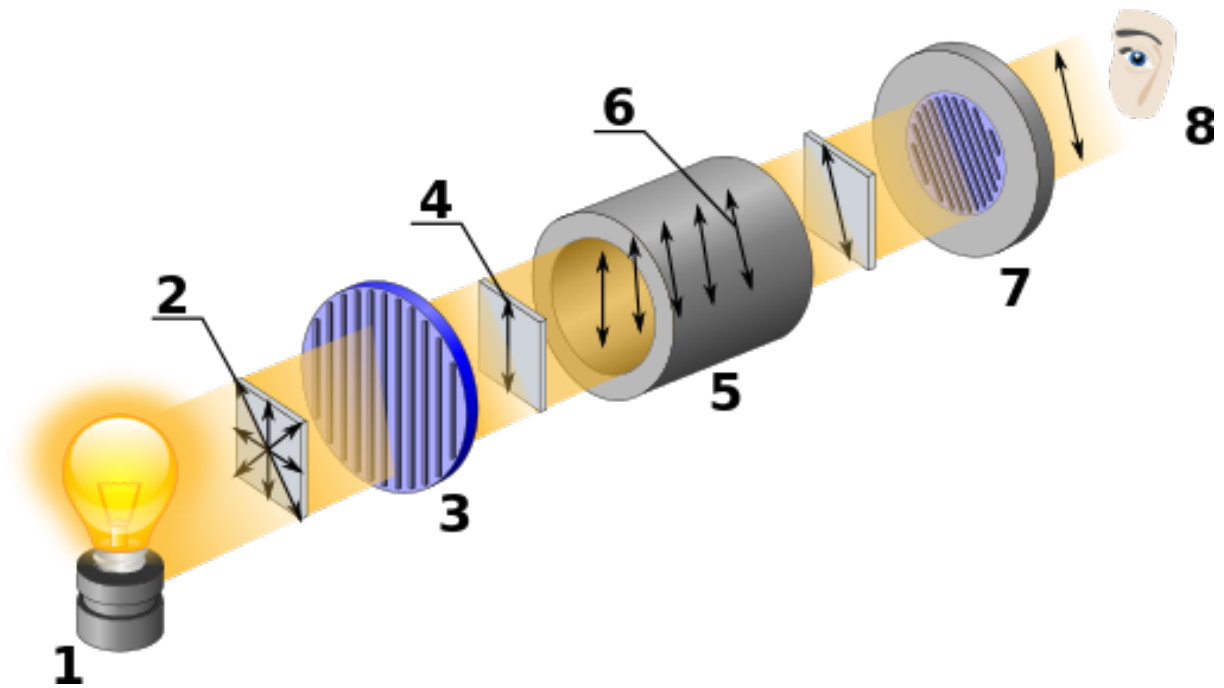
- El poder rotatorio específico es independiente de la distancia recorrida por la onda. Se define como:

$$\frac{\beta}{d} = \pi \frac{n_L - n_R}{\lambda}$$

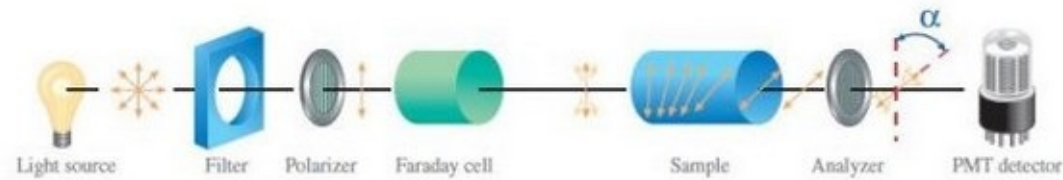
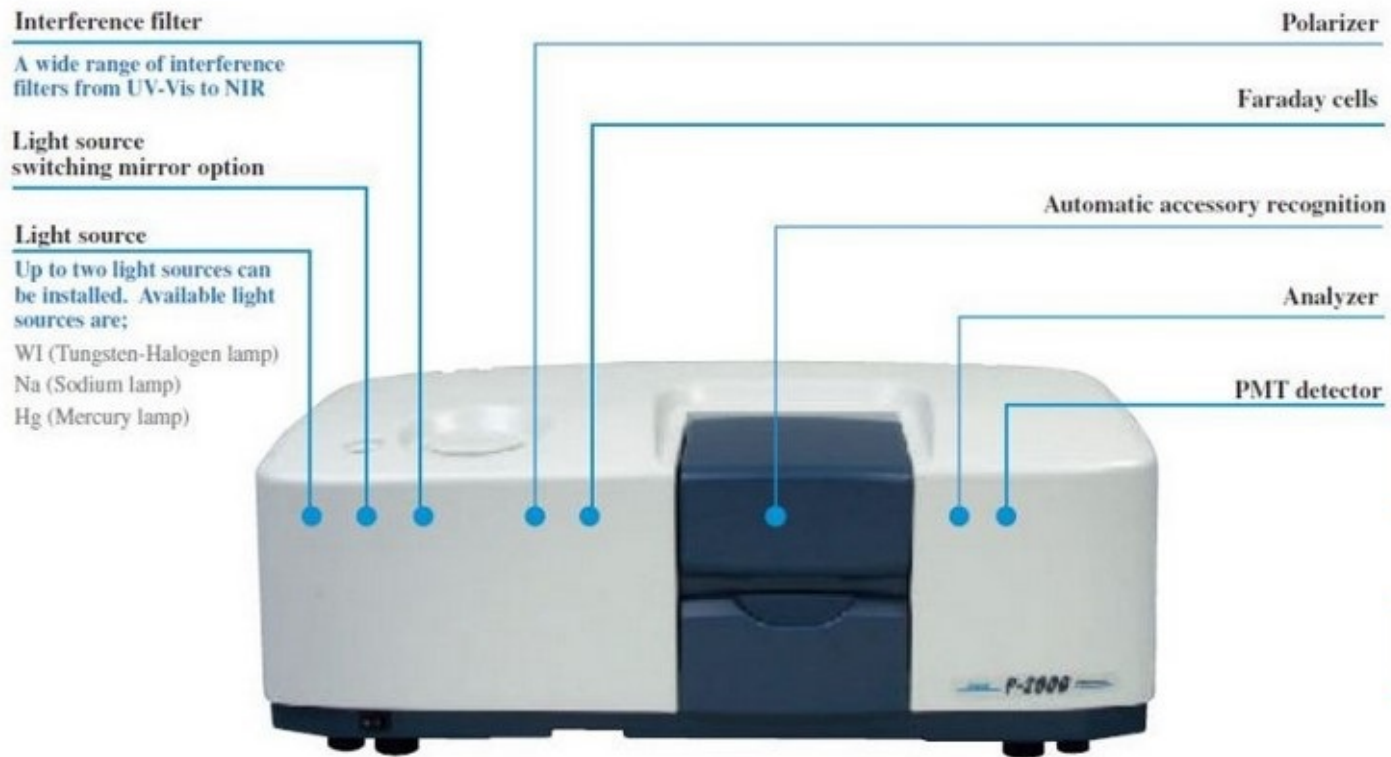
- En general se mide en $\frac{\circ}{mm}$ para sólidos y en $\frac{\circ}{cm}$ para líquidos
- Depende de λ . Usualmente referida al doblete del sodio a 25°C

El polarímetro: principio de funcionamiento

1. Fuente monocromática
2. No polarizada
3. Polarizador
4. Polarización vertical
5. Recipiente con muestra
6. Rotación
7. Analizador
8. Observador

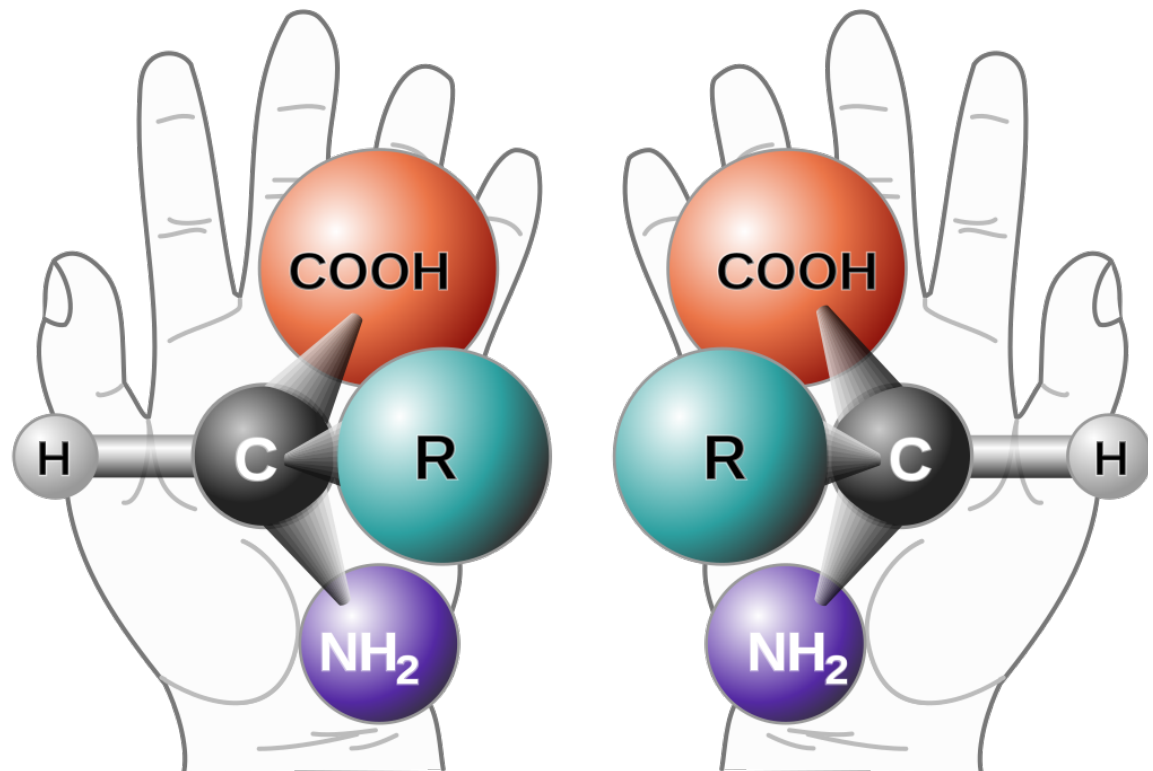


Polarímetro digital



Aplicaciones: estereoisómeros ópticos

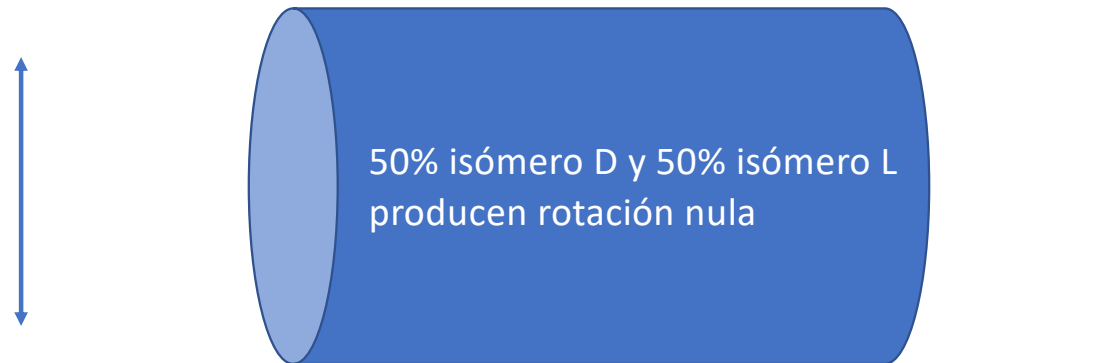
- Estereoisómeros ópticos son moléculas de igual composición pero de estructuras especularmente opuestas
- En 1848, Louis Pasteur diferencia estereoisómeros mediante el sentido de rotación de la polarización



Estereoisómeros

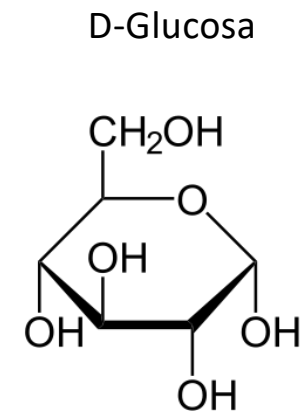
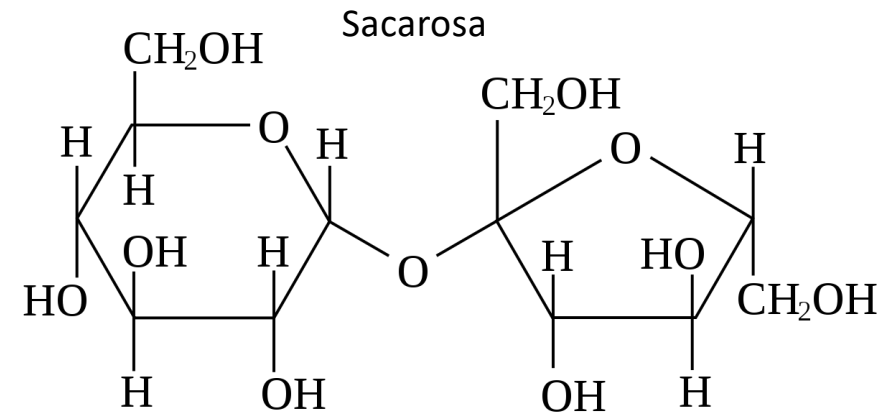
Aplicaciones: estereoisómeros ópticos

- El grado de rotación de la dirección de polarización depende de la concentración de un estereoisómero respecto al otro.



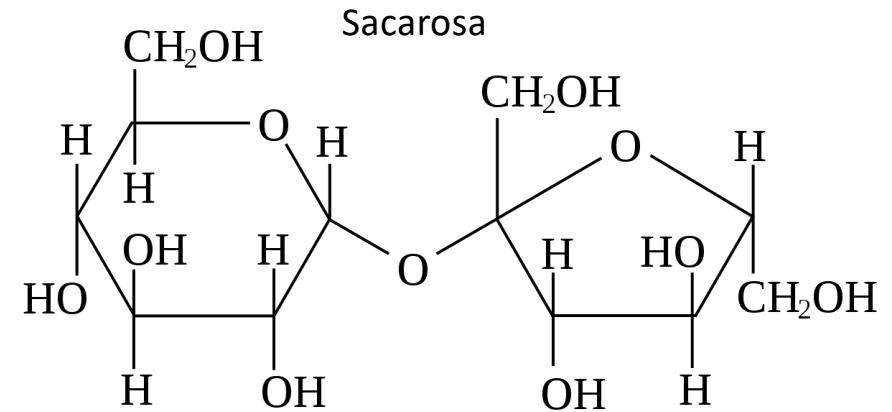
Sustancias biológicas ópticamente activas

- Cuando se sintetizan moléculas orgánicas en laboratorios se genera igual cantidad de isómeros-L y D.
- Esto no ocurre en la naturaleza.
- Por ejemplo el azúcar o sacarosa ($C_{12}H_{22}O_{11}$) nunca aparece en forma L, siempre en forma D.
- Otro ejemplo es la D-Glucosa

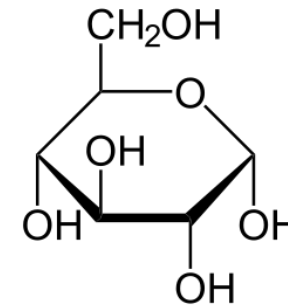


Sustancias biológicas ópticamente activas

- La mayoría de los aminoácidos son L-isómeros.
- Entre las excepciones importantes están los antibióticos.
- La Penicilina posee D-aminoácidos.



D-Glucosa



Prebiotic Evolution and Astrobiology

J. Tze-Fei Wong, PhD
Applied Genomics Center
Fok Ying Tung Graduate School
and
Department of Biochemistry
Hong Kong University of Science and Technology
Clear Water Bay, Hong Kong, China

Antonio Lazcano, PhD
Universidad Nacional Autonoma de Mexico
Mexico City, Mexico

Chirality, Homochirality and the Order of Biomolecular Interactions

Sandra Pizzarello*

7.1 Definition and Historical Background

Chirality is defined formally as the property of objects that cannot be brought into congruence with their mirror image by translation or rotation. The word derives from the Greek $\chi\epsilon\iota\rho$ that means hand and, in fact, the familiar name of “handedness” may explain this property more readily. Like the hands, chiral objects are found in two forms that are mirror images of each other and are identical in their component parts but do not match when super-imposed because these parts have a different spatial distribution. Trying to put a right hand in a left hand glove or a left foot in a right foot shoe will give a convincing demonstration. Chirality is widespread in nature in a variety of two- and tri-dimensional forms (Fig. 7.1) and can also be associated with motion, for example, when an object describes a helix that can equally cross left to right or right to left such as in a screw.

A script looked in a mirror gives a good illustration of chirality, as well as a hint on how to detect it (Fig. 7.1A). Letters that are symmetrical about a line or a point (H, O, I, etc.) will be the same on the script or the mirror (i.e., not chiral), while the ones that are asymmetric (C, L, R, etc.) look different in the mirror and are chiral. Of the three dimensional forms shown in the figure, tartrate crystals (Fig. 7.1B) are chiral for the different distribution of their asymmetric surfaces and have historical importance, as they were the first organic molecules discovered to give chiral structures by Louis Pasteur (1822-1895).¹ Pasteur was an eclectic and pioneering experimental scientist in many fields and, early in his career, came to analyze the crystals that commonly deposit at the bottom of wine barrels as tartar, as it was called, which was known to be made up of tartaric acid salts. He found that these salts could crystallize in the two mirror-image forms shown in the figure when synthesized in the laboratory but gave only one of the two when formed naturally during wine processing. This appeared at first contradictory, because both types of crystals had the same chemical formulas, but Pasteur had the insight to frame his observations on the basis of the discoveries of polarized light and its interaction with matter that had taken place during the 17th and early 18th centuries.

If we consider light as a wave motion of magnetic and electric fields oscillating in planes perpendicular to each other and to their line of propagation (Fig. 7.2A, H and E respectively), these oscillations will occur in innumerable planes when light is not filtered (Fig. 7.2B, viewed from a point along this line). However, light is found to emerge polarized on a single plane after passing through a transparent crystal of the mineral calcite (Fig. 7.2C). It has also been shown that the plane of this polarized light is rotated by passage

through certain “optically active” substances. By experimenting with tartrate crystals, Pasteur came to demonstrate that solutions of the natural, one-handed tartrate crystals were the only ones to rotate polarized light while a mixture of the two forms did not. In doing so, he made two profound discoveries: that organic molecules, not just crystals, can have two spatial structures and that terrestrial biomolecules show only one handedness—that is, they are chirally homogeneous or homochiral as it was later determined.

7.2 Chiral Asymmetry of Organic Compounds and Biological Homochirality

As we know now, in fact, a common and most interesting case of chirality is that displayed by the compounds of carbon (C). This element has four binding valences and the spatial distribution of its bonds is such that a C in a molecule can be visualized as a regular tetrahedron with C at its center and the four bonded groups at the vertices (Fig. 7.1C,D). When all these groups differ, the C becomes asymmetric (C*) and the molecules that contain such a carbon atom are chiral, i.e., they can exist in two “handed” forms called enantiomers. The enantiomers of a chiral molecule have matching chemical properties and will interact equally with nonchiral molecules and structures. However, they do not have identical physicochemical properties, because of the different spatial distribution (configuration) of the chiral carbon substituents groups and the different polarizability of its electrons that this difference entails. For example, solutions of the two enantiomers of a chiral molecule will rotate polarized light in opposite directions and it is only when they are present in equal amounts and compensate each other's effect that solutions become optically inactive (this equal mixture of enantiomers is called racemic, as the synthetic tartaric acid Pasteur analyzed). Figure 7.1D, gives the Fisher projection formula of glyceraldehyde, which is the simplest chiral sugar whose enantiomers are designated by convention as D- and L-, from being dextro-rotatory and levo-rotatory for polarized light, respectively. Glyceraldehyde is also the reference compound in the designation of other sugar and amino acid enantiomers.

One difference between enantiomers, which derives from the above properties and is most important to biochemistry, is that they will interact differently with other chiral molecules. Even for the same compound, enantiomers will behave differently upon encountering enantiomers of the same or opposite configuration, for example, the interaction/reaction of an L-amino acid with its L- or D-enantiomer will differ and the interacting DD and DL complexes will have different energies.

*Sandra Pizzarello—Department of Chemistry and Biochemistry, Arizona State University, Tempe Arizona 85287-1604 USA.
Email: pizzar@asu.edu