Optical spectroscopy in materials science 6.
Spectroscopic methods based on anisotropy

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Optical anisotropy

- χ, ε, n are tensors
- if the medium is not isotropic, there is different response to excitations of different polarization

Polarization	Quantity	Notation	
linear	*n’*	**(linear) birefringence** ***(lineáris) kettőstörés***	
linear	*n”*	**(linear) dichroism** ***(lineáris) dikroizmus***	
circular	*n’*	**optical rotation** ***optikai forgatás***	**optical activity** ***optikai aktivitás***
circular		**Or: circular birefringence** ***cirkuláris kettőstörés***	
	n”	**circular dichroism** ***cirkuláris dikroizmus***	

Optical activity

Optical rotatory dispersion (ORD): different index of refraction for left and right circularly polarized light

↓

polarization plane of linearly polarized light will rotate

Circular dichroism: extinction coefficient different

↓

linearly polarized light changes into elliptical

Optical rotation

angle of rotation:

$$\theta = (n_L' - n_R')\frac{\omega l}{2c} = \alpha l$$

c velocity of light

$$\frac{\theta}{l} = \alpha = (n_L' - n_R')\frac{\omega}{2c} = (n_L' - n_R')\frac{\pi}{\lambda}$$

specific rotation (for solutions) :
fajlagos forgatóképesség

$$[\alpha] = \frac{\theta}{lc'}$$

c' concentration

Important!

λ = 589 nm (Na D-line)
T = 25 °C
solvent: water
[c']: g/100 cm^3
[ℓ]: dm

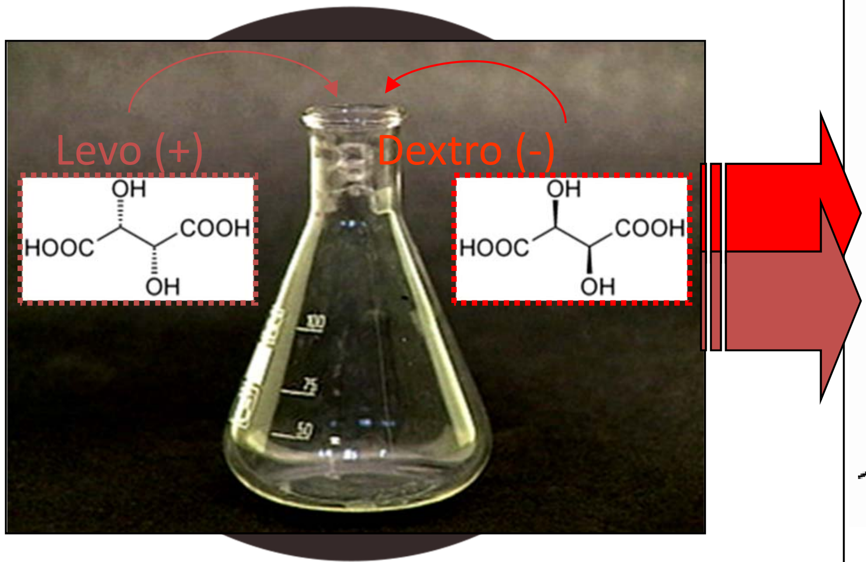
Application: sugar concentration
(health system, food industry)
polarimetry, sacharimetry

Natural optical rotation

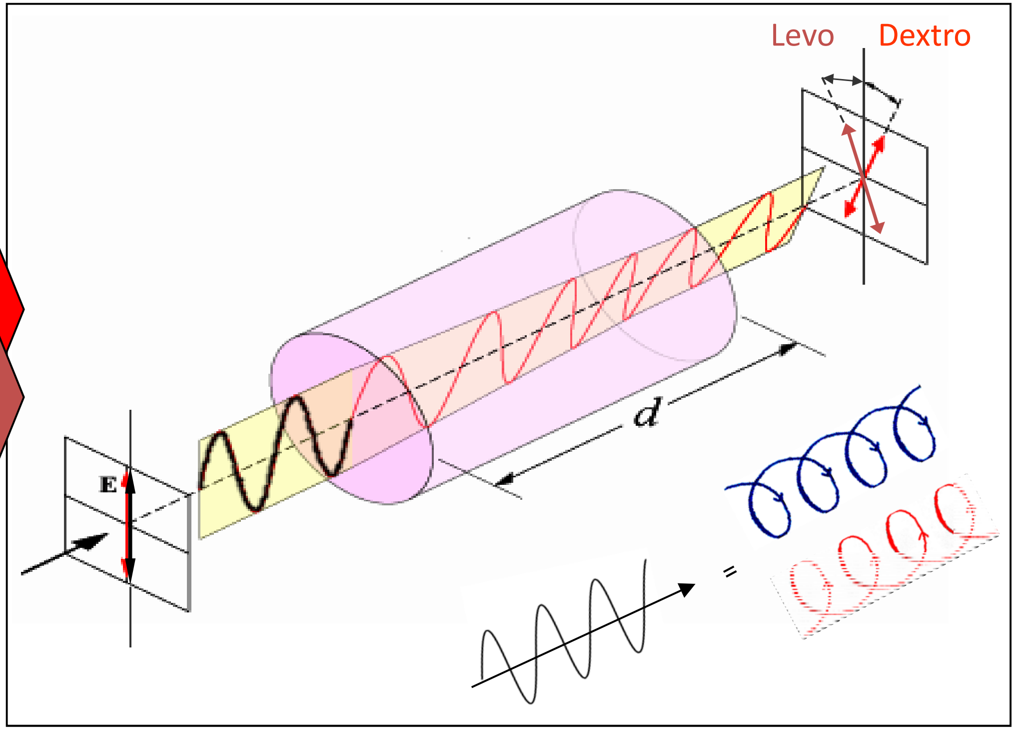
Kézsmárki István, BME Fizika Tsz

tartaric acid

Pasteur (1849)



Optical rotation



Circular dichroism

Ellipticity: *n”* different → absorption different → $\Delta\varepsilon \sim \Psi$

$$\frac{\phi}{l} = \Psi = \frac{\pi}{\lambda}(n_L'' - n_R'')$$

ϕ ellipticity, Ψ ellipticity created on 1 cm pathlength

specific ellipticity
fajlagos ellipticitás:

$$[\Psi] = \frac{100\phi}{lc'}$$

also used: difference in extinction (absorption) coefficient:
(specific, molar)

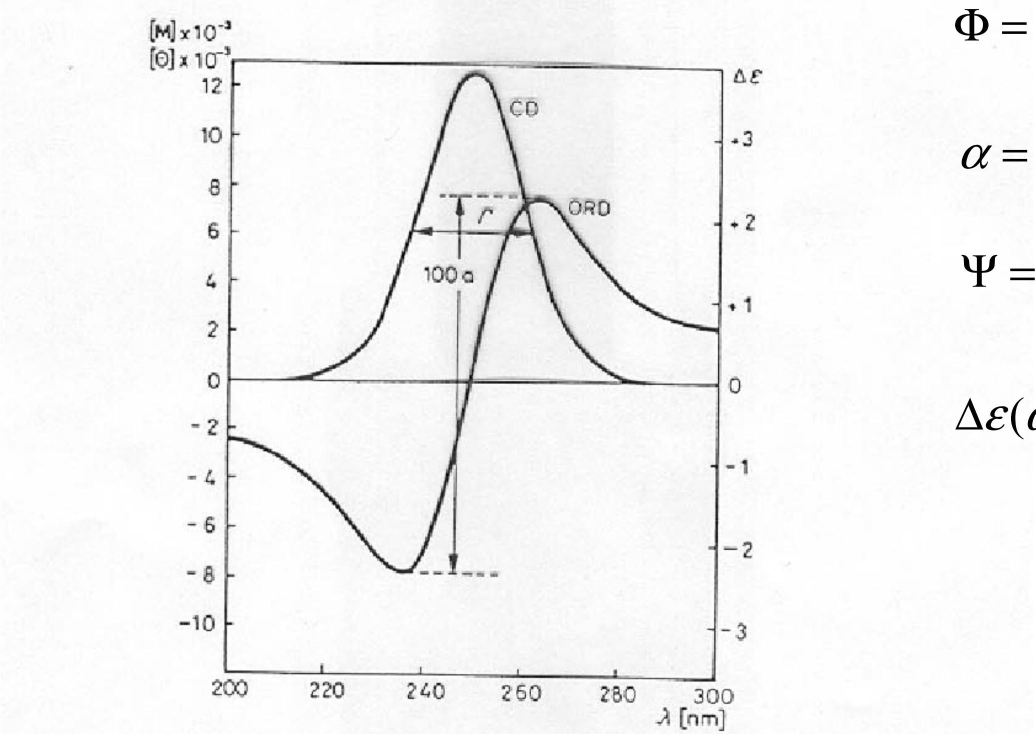
$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R \cong n_L'' - n_R''$$

Summarized in one quantity:

$$\Phi = \alpha + i\Psi = \frac{\pi}{\lambda}(\tilde{n}_L - \tilde{n}_R)$$

Definition of R, L and sign is arbitrary!

Cotton effect



Pozitív Cotton-effektusnak megfelelő (idealizált) CD- és ORD-görbepár ($R = 0{,}1$ D μ_B
$\Gamma = 25$ nm, $\lambda_{max} = 250$ nm)

$$\Phi = \alpha + i\Psi = \frac{\pi}{\lambda}(\tilde{n}_L - \tilde{n}_R)$$

$$\alpha = \frac{\pi}{\lambda}(n_L' - n_R')$$

$$\Psi = \frac{\pi}{\lambda}(n_L'' - n_R'')$$

$$\Delta\varepsilon(\omega) = \frac{4}{c_0 \log 10}\Psi(\omega)$$

α and Ψ are related
by Kramers-Kronig relations

Positive Cotton effect: $\Psi > 0$
Negative: $\Psi < 0$

Microscopic picture

excitation ⟶ structure ⟶ ring current ⟶ magnetic field ⟶ magnetic field of light

$$\mathbf{D} = \varepsilon\mathbf{E} - g\sqrt{\varepsilon_0\mu_0}\,\dot{\mathbf{H}} \qquad \mathbf{B} = \mu_0\mathbf{H} + g\sqrt{\varepsilon_0\mu_0}\,\dot{\mathbf{E}}$$

$$n_{L,R} = \sqrt{\varepsilon_{rel}} \pm g\omega$$

g *z*-component of (macroscopic) giration vector

β is the microscopic parameter corresponding to g

$$\beta = \frac{c}{3\pi\hbar}\sum_j \frac{R_{ij}}{\omega_{ij}^2 - \omega^2}$$

R_{ij} is the *molecular rotatory strength* corresponding to the given excitation: $R_{ij} = \mathrm{Im}\left\{\langle i|\boldsymbol{\mu}|j\rangle\langle j|\mathbf{m}|i\rangle\right\}$

$$\mu = \alpha\mathbf{E} - \frac{\beta}{c}\dot{\mathbf{H}} \qquad m = \frac{\beta}{c}\dot{\mathbf{E}}$$

α here polarizability!

R_{ij} differs from zero if *both* electric (μ) and magnetic (m) dipole change!

Applications

- information about optical isomers (identical structure, except for rotation)
- resolution can be increased in some cases(sign!)
- magnetic dipole transitions can increase intensity

- ORD: in the whole frequency range
- CD: only around excitations

Measurement: dichrograph – piezoelectric modulator

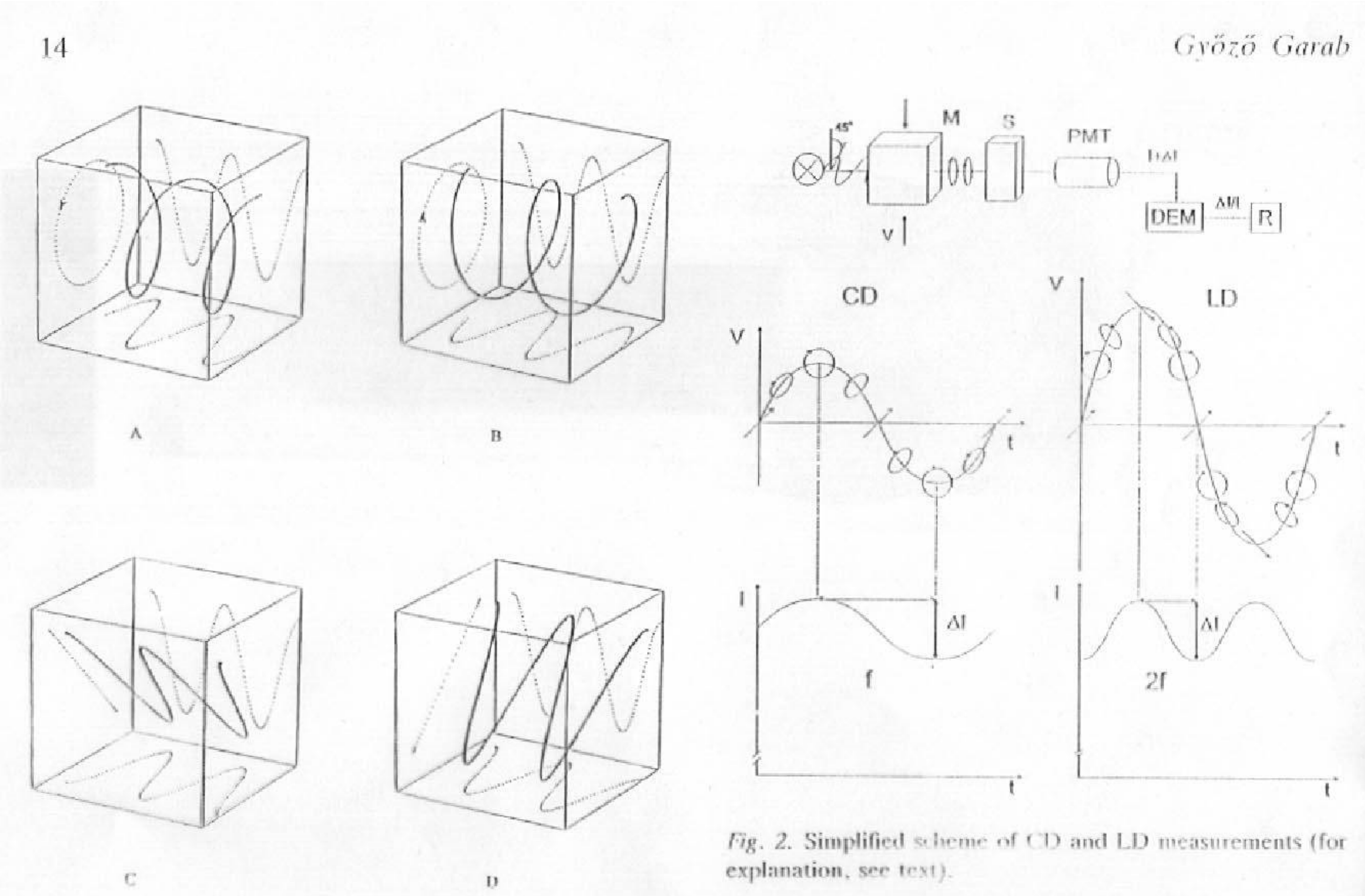


Fig. 2. Simplified scheme of CD and LD measurements (for explanation, see text).

Measured quantity:
T
↓
log T ⟶ ΔI/I ~ΔA

Incident light linearly polarized (45°)

modulator changes index of refraction in one direction on applied voltage

Garab Győző, SZBK

Optical isomerism

Structural condition: chirality
(lack of symmetry element S_n)

Optical isomerism:

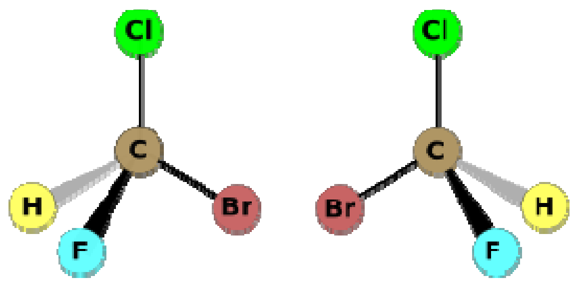
• *enantiomers:* can be transformed into each other by reflection across a plane

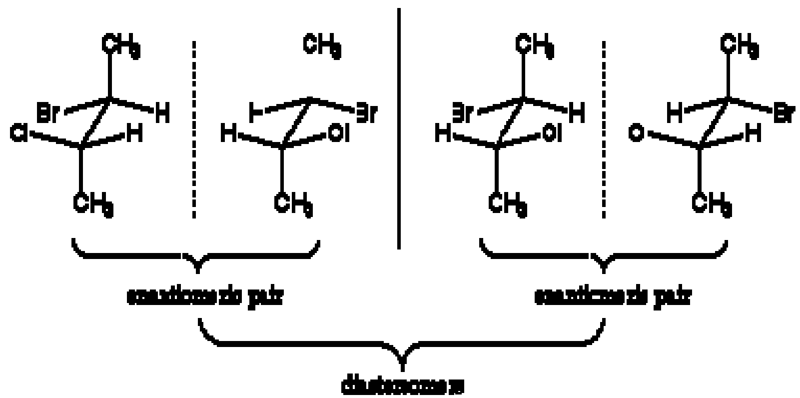
• *racemic mixture (racém keverék):* mixture of enantiomers in a 1:1 ratio

• *diastereomers:* isomers formed by the reaction of two chiral molecules (*not enantiomers)*

http://en.wikipedia.org/wiki/Chirality_(chemistry)

enantiomers

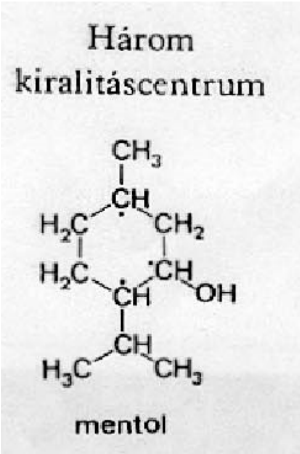




http://www.sparknotes.com/chemistry/organic3/enantiomersanddiastereomers/section2.rhtml

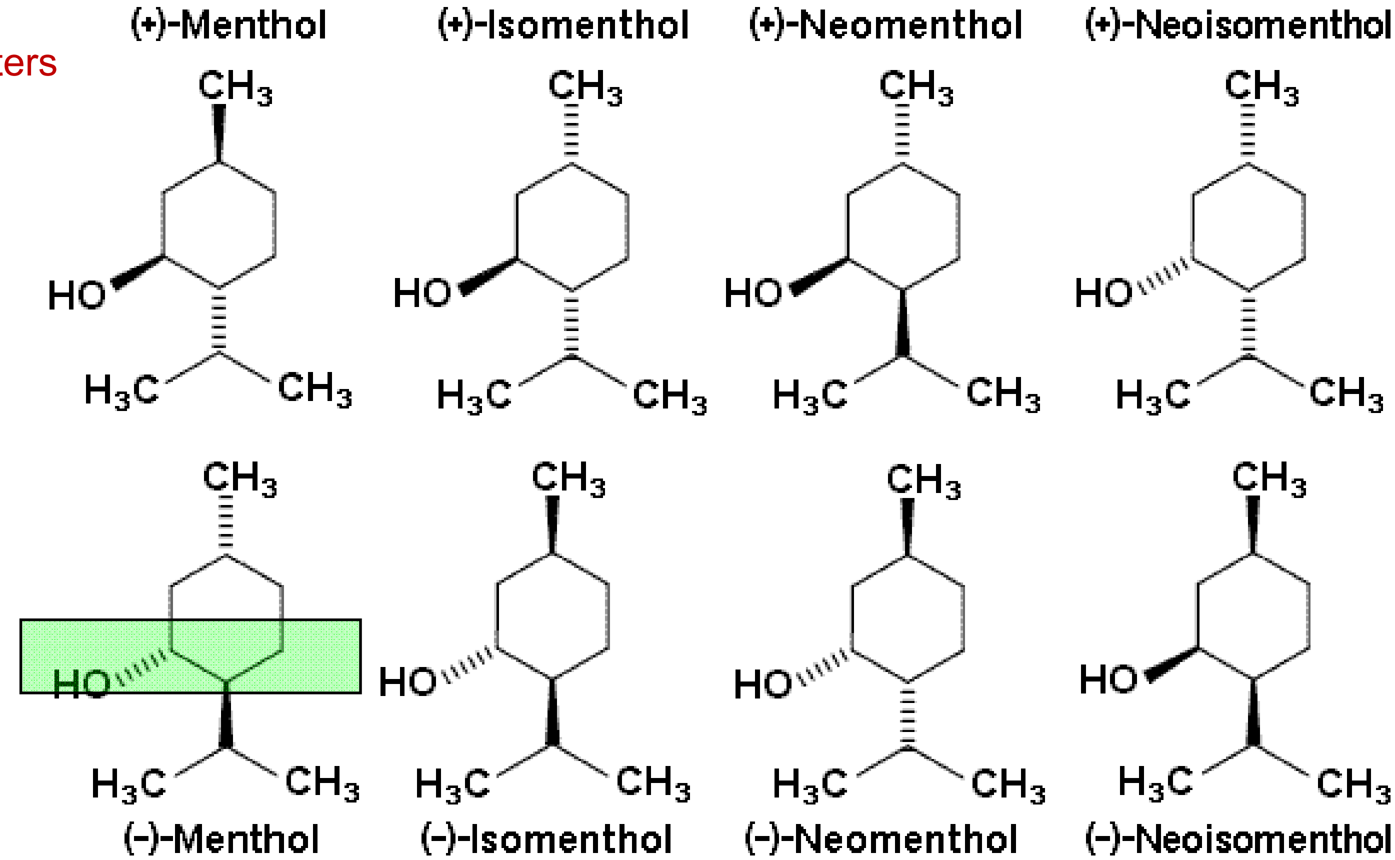
Optical isomerism

Three chirality centers



menthol

Kajtár Márton: Változatok négy elemre



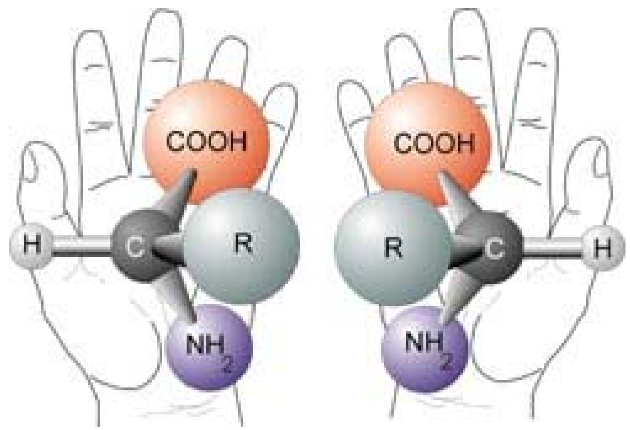
http://en.wikipedia.org/wiki/Image:Menthols.PNG

Separation of optical isomers

Separation of optical isomers:
symmetric synthesis ⟶ diastereomers

Natural substances (enzymes, amino acids):
only one enantiomer exists
(*nature is chiral)*

Application: age determination
(amino acid racemization)



http://www.nai.arc.nasa.gov/