Optical spectroscopy in materials science 6.
Practical KK transformation and 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:

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

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

specific rotation (for solutions) :
fajlagos forgatóképesség

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

Important!

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

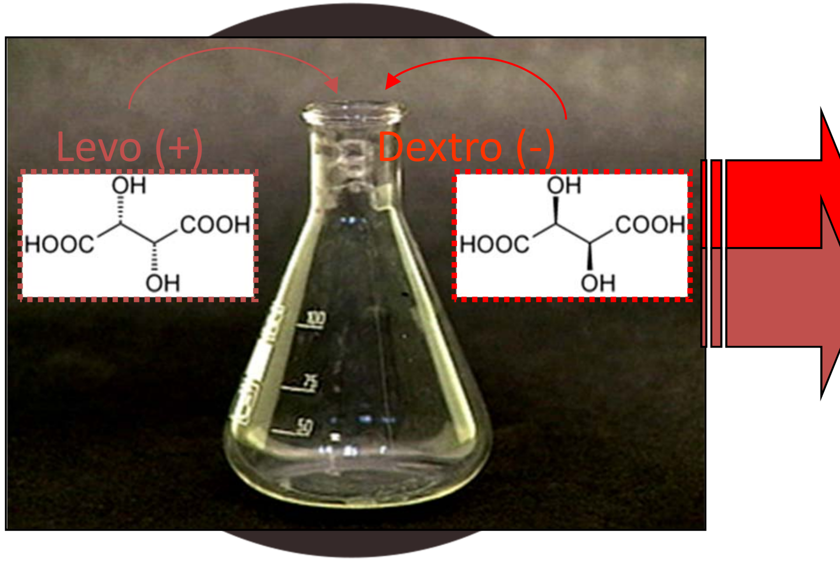
Application: sugar concentration (health system, food industry)
polarimetry, sacharimetry

Natural optical rotation

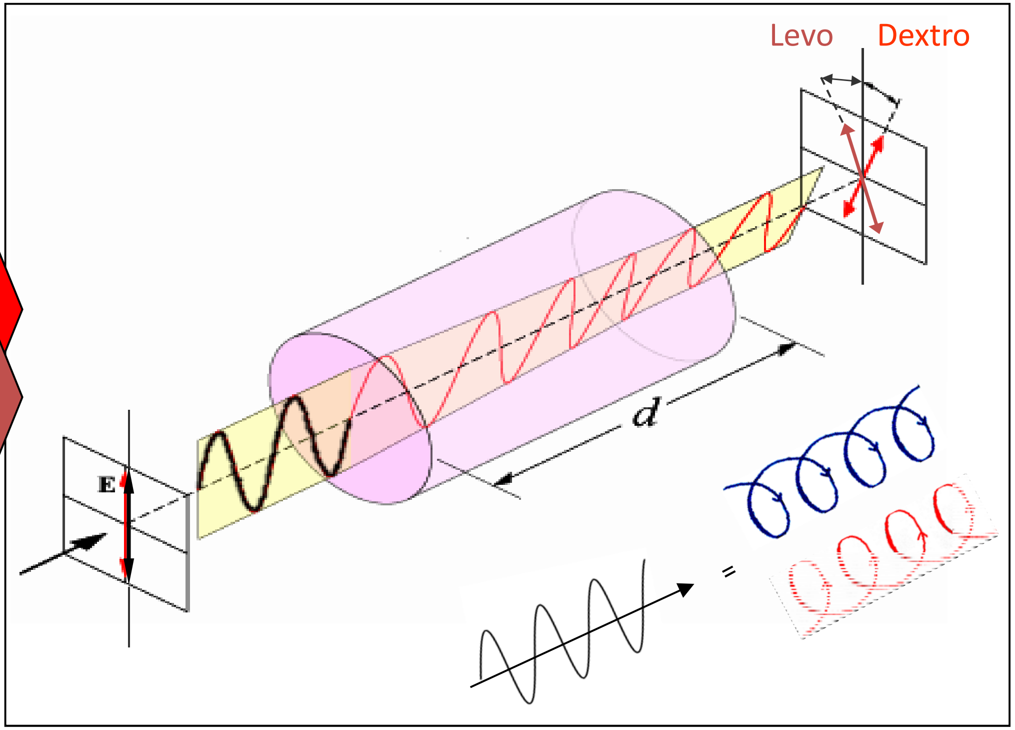
Kézsmárki István, BME Fizika Tsz

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)

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

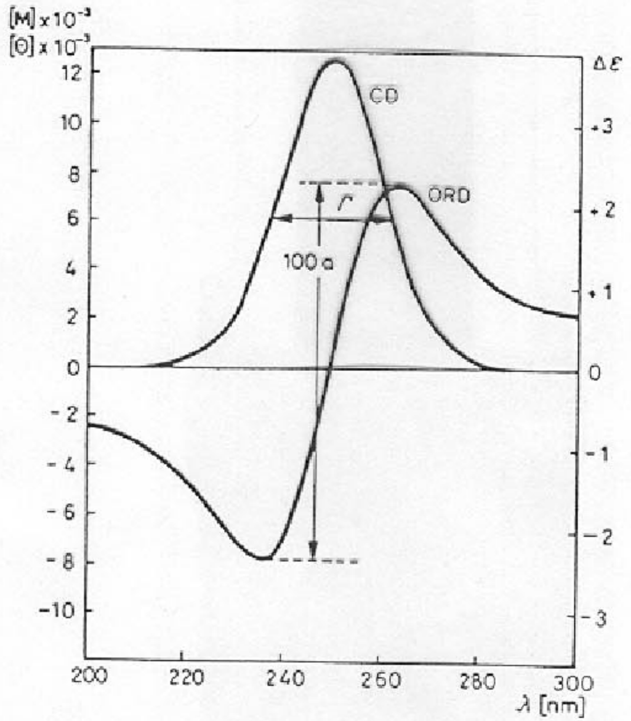
$$\Delta\varepsilon(\omega) = \frac{4}{c_0 \log 10}\Psi(\omega)$$

Summarized in one quantity:

$$\Phi = \alpha + i\Psi = \frac{\pi}{\lambda}(n_L - n_R)$$

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)

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

α and Ψ are related
by Kramers-Kronig relations

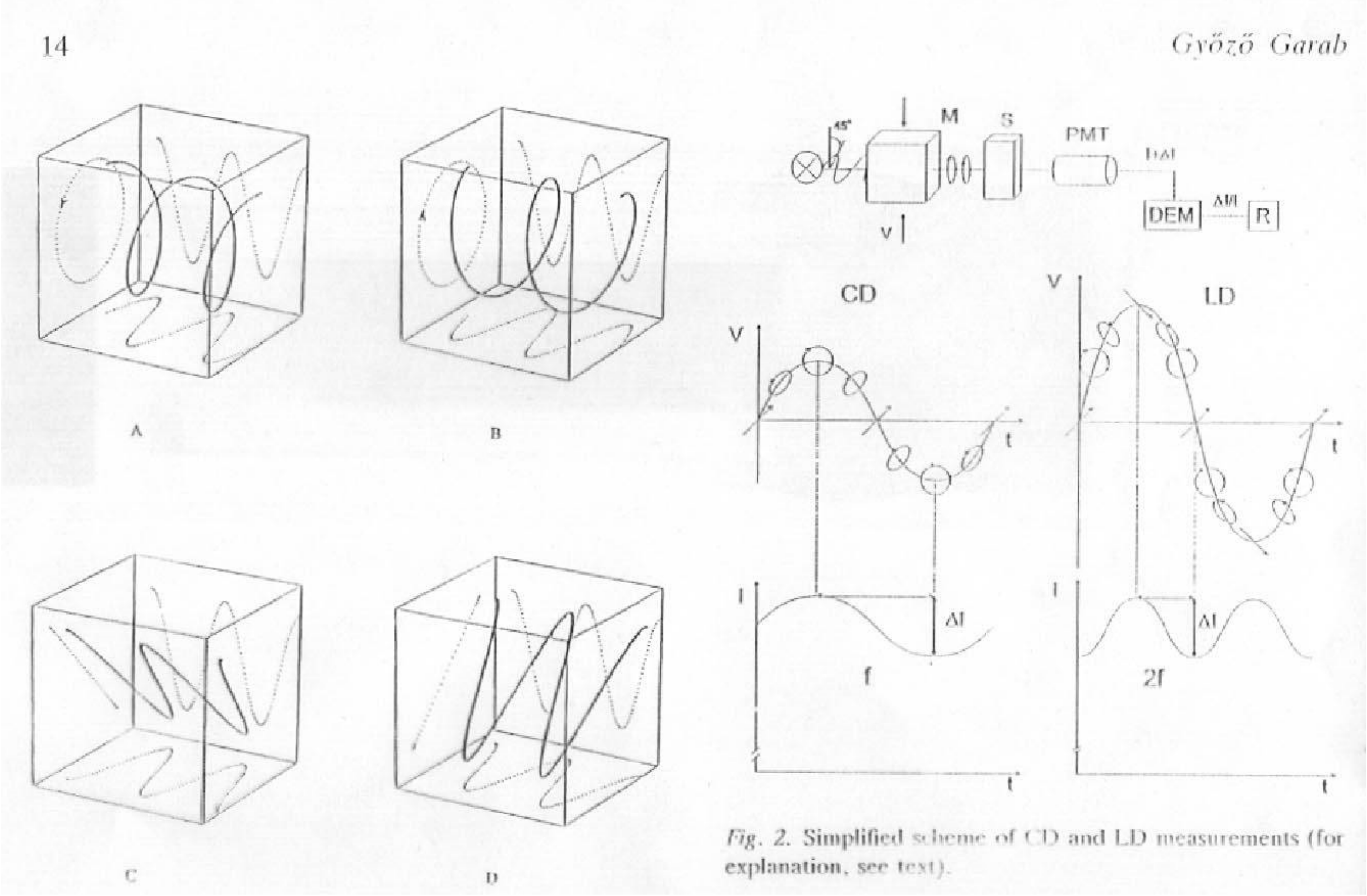
Positive Cotton effect: $\Psi > 0$
Negative: $\Psi < 0$

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



14 Győző Garab

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

Measured quantity:
T
↓
log T ⟶ $\Delta I/I \sim \Delta A$

Incident light linearly polarized (45°)

modulator changes index of refraction in one direction on applied voltage

Garab Győző, SZBK

Optical isomerism

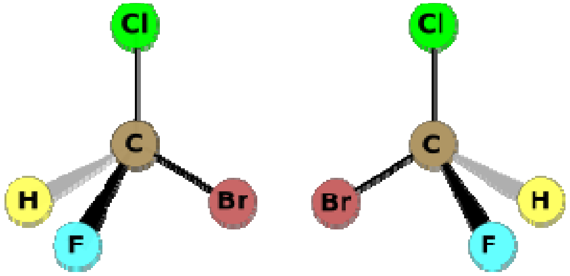
Structural condition: chirality
(lack of symmetry element S_n)

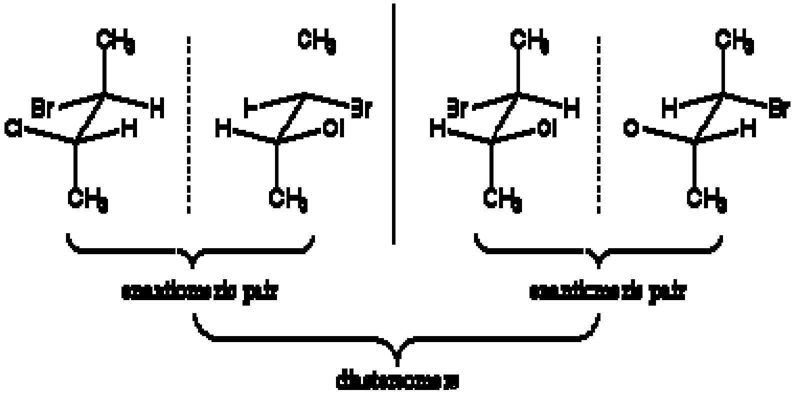
Optical isomerism:

- *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

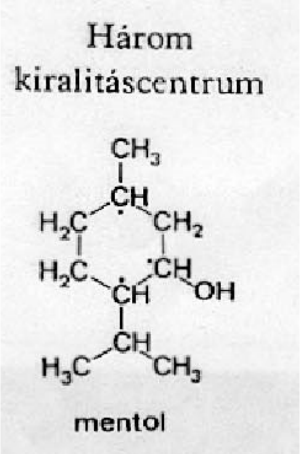




http://www.sparknotes.com/chemistry/organic3/enantiomersanddiastereomers/section2.rhtml

Optical isomerism

Three chirality centers

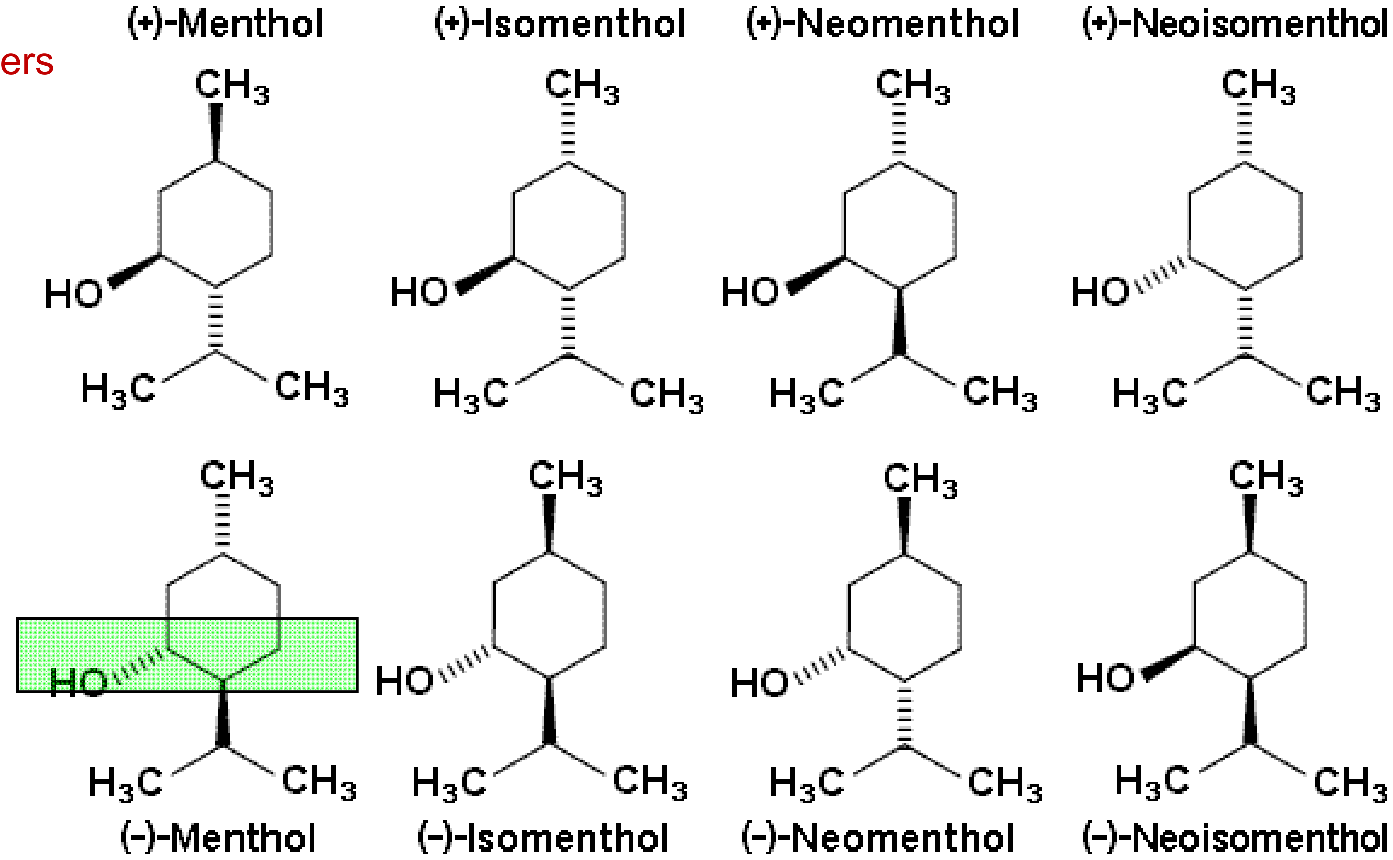


Három kiralitáscentrum

mentol

menthol

Kajtár Márton: Változatok négy elemre



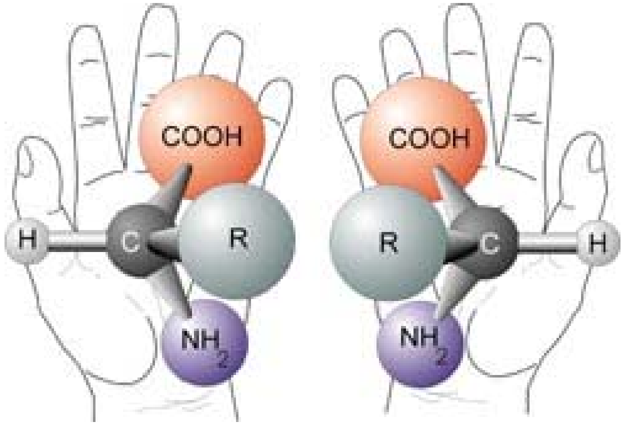
http://en.wikipedia.org/wiki/Image:Menthols.PNG

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/

Reflectance spectroscopy

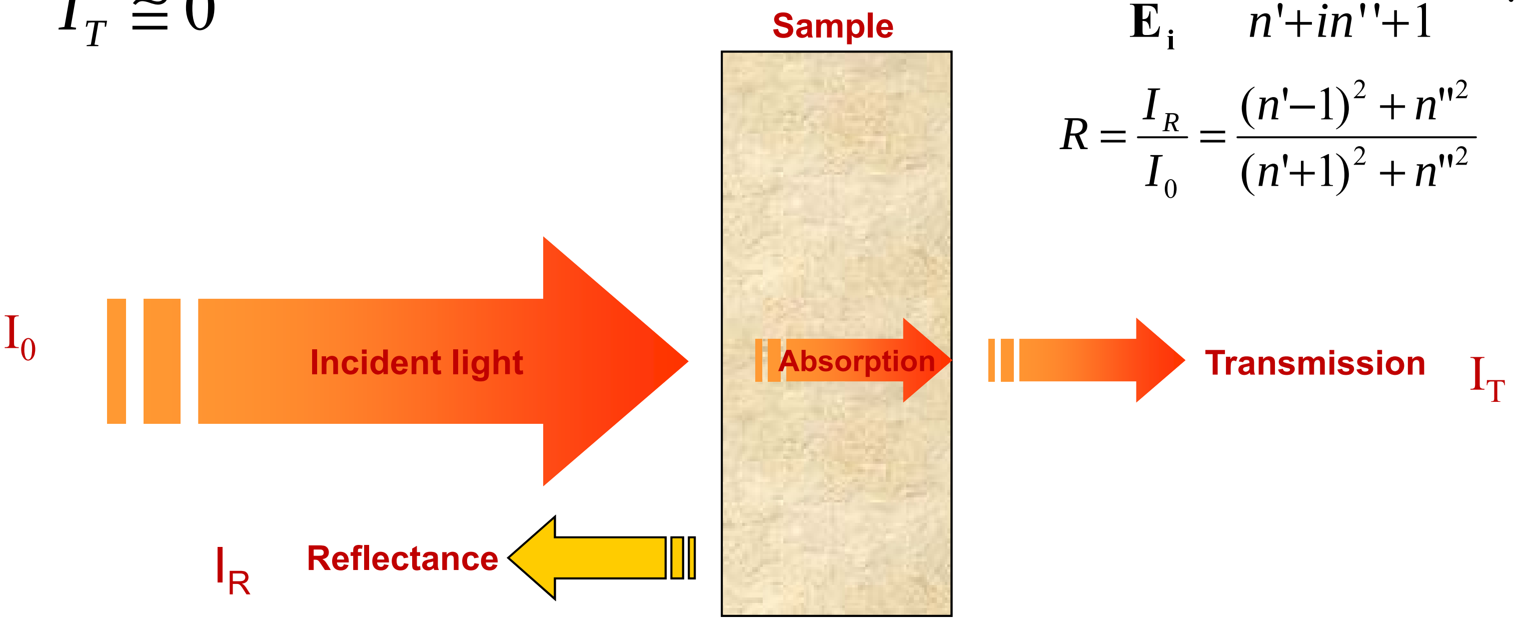
$$I_0 = RI_0 + (1-R)I_0 e^{-\alpha d} + I_A$$

$$I_T \cong 0$$

Fresnel equations for normal incidence:

$$r = \frac{\mathbf{E_r}}{\mathbf{E_i}} = \frac{n' + in'' - 1}{n' + in'' + 1} = \sqrt{R}e^{i\theta}$$

$$R = \frac{I_R}{I_0} = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2}$$



Reflectance spectroscopy

Dispersion relations - reflectance

$$r = \frac{\mathbf{E}_\mathbf{r}}{\mathbf{E}_\mathbf{i}} = \frac{n'+in''-1}{n'+in''+1} = \sqrt{R}e^{i\theta} \qquad \ln r = \frac{\ln R}{2} + i\theta$$

11.51 egyenlet hibás!
(-1-szerese)

ln *r* is also a good transfer function, dispersion relations hold
measured quantity: R(ω)

Kramers-Kronig (KK) transformation:

$$\theta(\omega) = -\frac{\omega}{\pi}\mathbf{P}\int_0^\infty \frac{\ln R(\xi)}{\xi^2-\omega^2}d\xi = \frac{-1}{2\pi}\mathbf{P}\int_0^\infty \ln\left|\frac{\xi+\omega}{\xi-\omega}\right|\frac{d\ln R(\xi)}{d\xi}d\xi$$

Contribution to θ: ξ-ω small or dlnR/dξ large

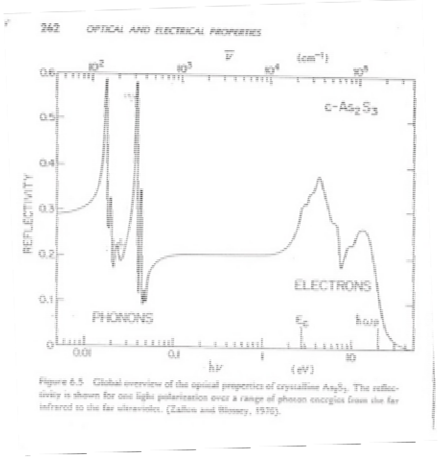

262 OPTICAL AND ELECTRICAL PROPERTIES

Figure 6.5 Global overview of the optical properties of crystalline As₂S₃. The reflectivity is shown for one light polarization over a range of photon energies from the far infrared to the far ultraviolet. (Zallen and Blossey, 1976).

KK analysis: extrapolations

$\omega \rightarrow 0:$

- known σ(dc): fitting, smoothing
- semiconductors, bound electrons: constant R

$\varepsilon'' = 0$, ε' can be calculated from R

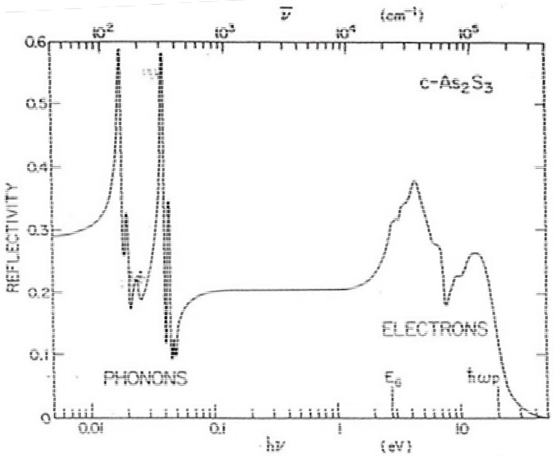


Figure 6.5 Global overview of the optical properties of crystalline As_2S_3. The reflectivity is shown for one light polarization over a range of photon energies from the far infrared to the far ultraviolet. (Zallen and Blossey, 1976).

$\omega \rightarrow \infty:$

asymptotic limit (free electrons):

$$R \sim \left(\frac{\omega}{\omega_p}\right)^{-4}$$

reflectance of plasma ($\omega > 10^6$ cm^{-1}, all electrons excited)

intermediate region: $$R \sim \left(\frac{\omega}{\omega_p}\right)^{-S}$$

S (and even ω_p) arbitrary, because we only want to approximate the integral, $R \sim \omega^{-S}$

KK analysis: extrapolations

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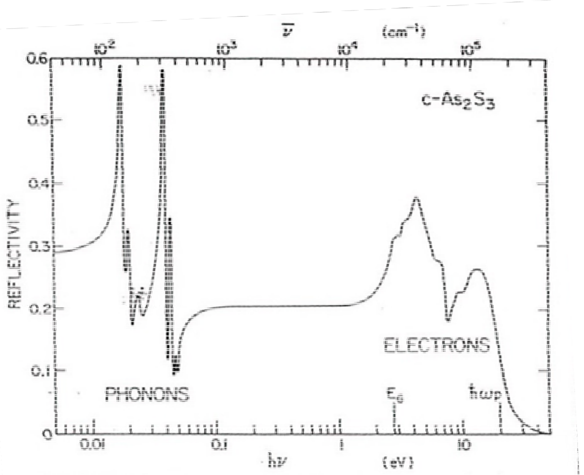

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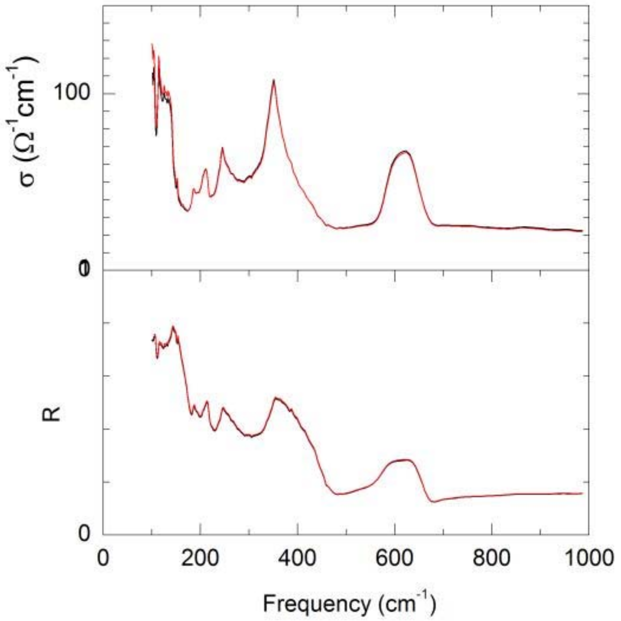
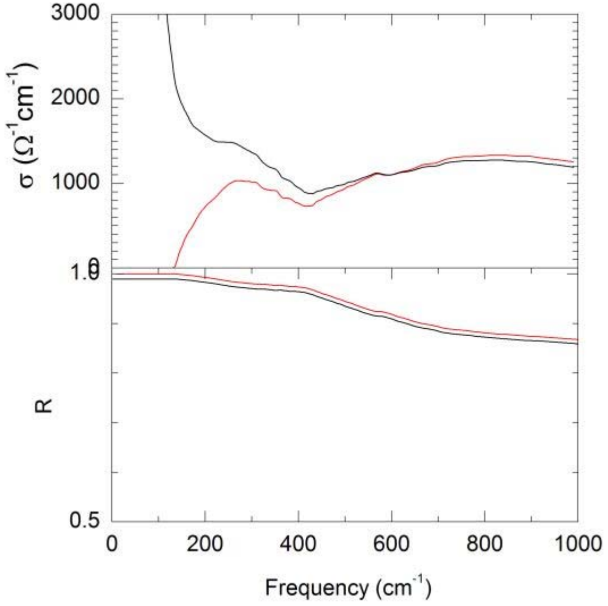
KK analysis: errors

$$R \cong 0, R \cong 1$$

$$n = \frac{1+r}{1-r}$$



Semiconductor



Superconductor

KK analysis: procedure

1. ε'' or σ (any extrapolation)
2. starting parameters (Drude-Lorentz ω_p, ω_0, γ)
3. fit to **measured** quantity (reflectance)
4. KK transformation with extrapolation from model

   frequency range: only **measured** range