Advanced Vitreous State – The Physical Properties of Glass

Passive Optical Properties of Glass

Lecture 1:

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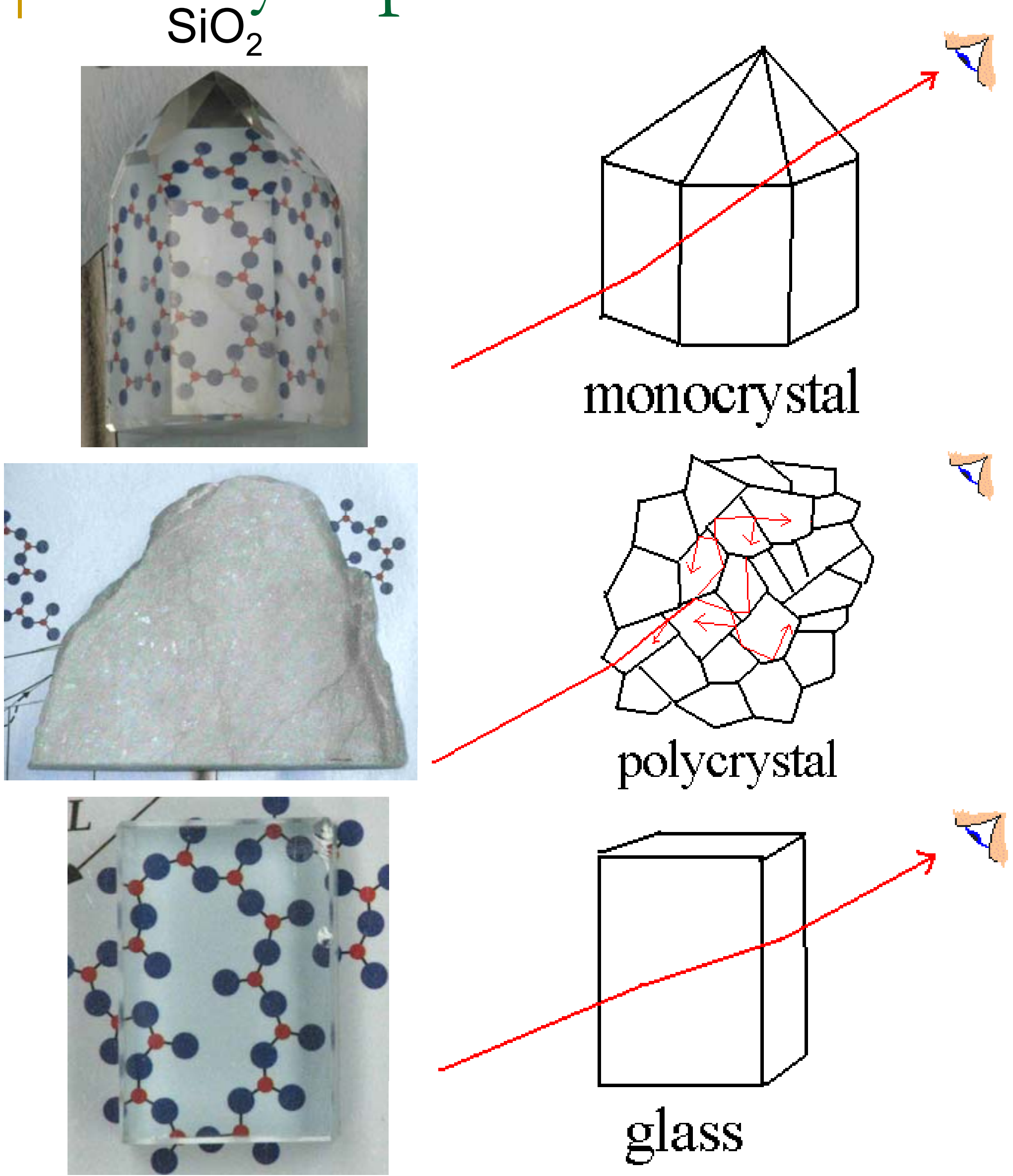
Glassy Optical Materials: Motivation



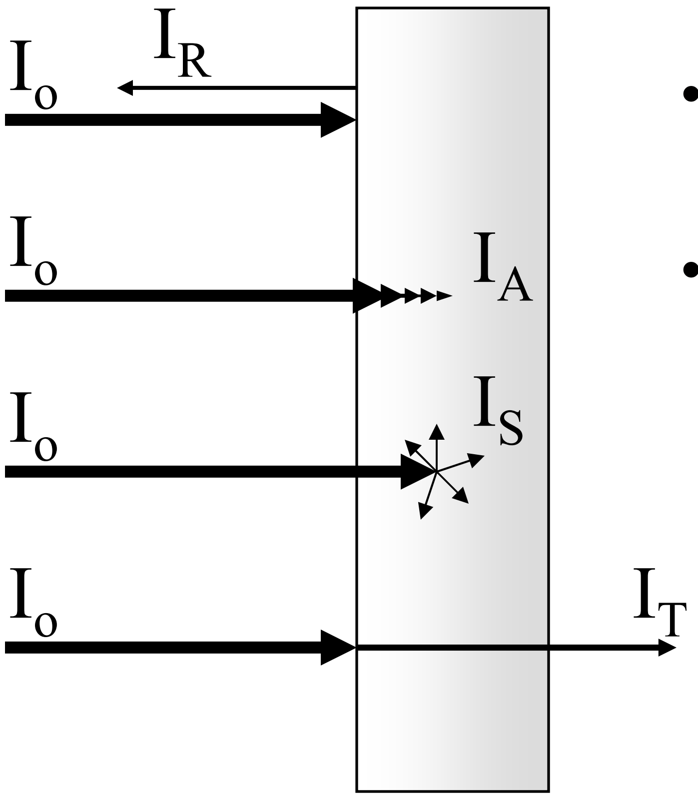
- Good optical properties
- Hard to synthesize

- Easy to synthesize
- Bad optical properties

- Good optical properties
- Easy to synthesize

Optical properties of materials

- Four things can happen when light proceeds into a solid.



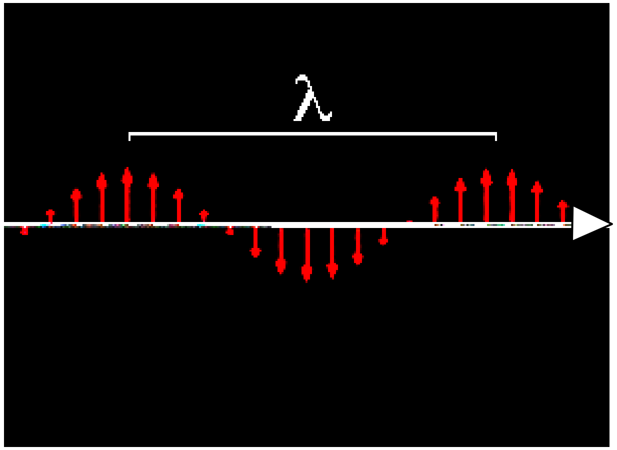
- Part of the light can be reflected by the surface of the solid. Reflection
- Part of the light can be absorbed by coupling into the solid. Absorption
- Part of the light can be scattered by the atoms and defects in the solid. Scattering
- Part of the light can be transmitted through the solid. Transmission

- Therefore, for an incident beam of intensity I_o entering the solid:

$$\mathbf{I_o = I_R + I_T + I_A + I_S}$$

Optical properties of materials:

- Light is an electromagnetic wave. An electric and magnetic field oscillating perpendicular to the direction of propagation.



- When light penetrates a solid, the oscillating electric field couples with dipoles created by charged particles (nucleus, electrons, ions) composing the solid.

- The mechanism and magnitude of this interaction varies for every materials and depends on its:
  - chemical composition
  - structural properties

- One parameter is sufficient to characterize entirely the optical properties: the complex refractive index $\mathbf{n}=n+i\kappa$

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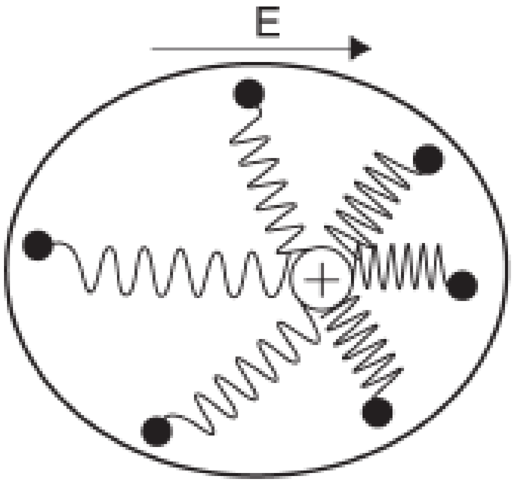
Origin of light-matter interaction

- Light can couple with **electronic oscillators**: electrons bound to nucleus



(a) Classical description of an electronic oscillator

m_e : mass of an electron

m_N : mass of a nucleus

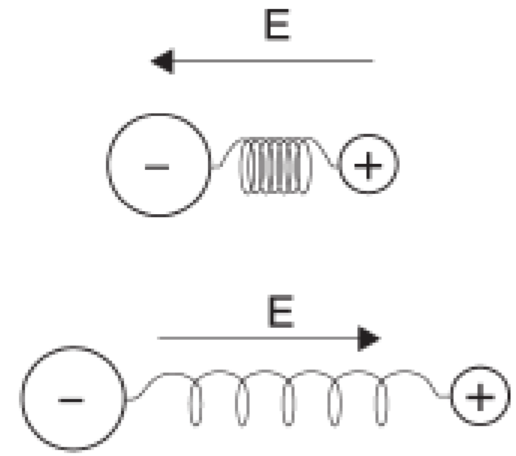
Reduced mass: $$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

Resonant frequency: $$\omega_0 \propto \sqrt{\frac{1}{\mu}}$$

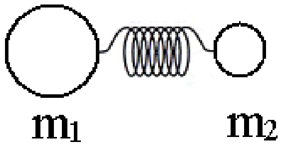
$m_N >> m_e$ and $\mu \approx m_e$, hence the small electronic mass of electrons determine the resonant frequency of electronic oscillator which is very high in the UV and visible region of the spectrum.

Origin of light-matter interaction

- Light can couple with **vibrational oscillators**: ionic bonds and some covalent bonds.



(b) Vibrational oscillator



Reduced mass: $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

Resonant frequency: $\upsilon = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$

Atomic mass are orders of magnitude larger than the mass of electrons hence the resonant frequency of vibrational oscillator is low, typically in the infrared region of the spectrum.

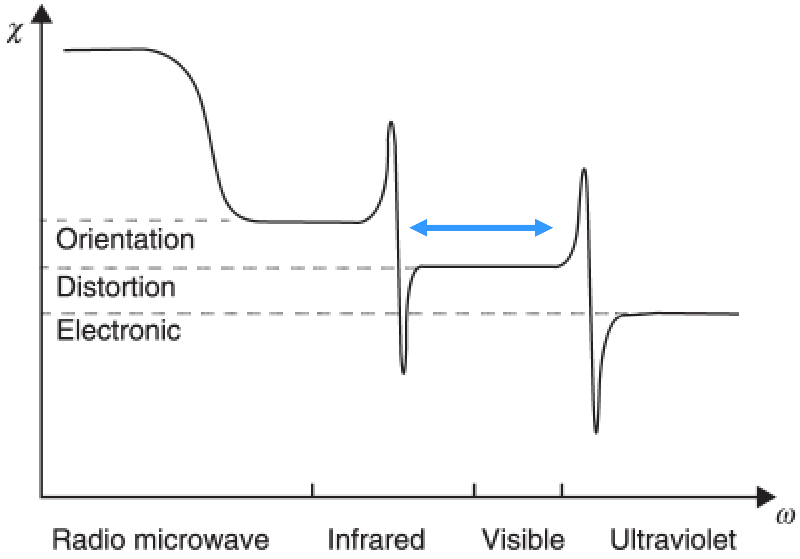
Polarization

- Hence a material gets polarized under the action of the electric field of an electromagnetic wave (light).

The ability of the material to polarize is expressed as the dielectric susceptibility: χ

$$P = \varepsilon_0 \chi E$$

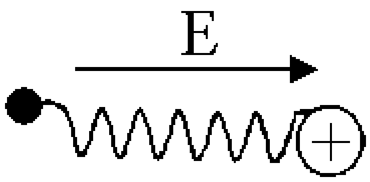
It is the proportionality constant between the disturbing field E and the materials response, the polarization P.



In a solid glass, there is no rotational degree of freedom, hence no contribution from dipole orientation. But there is distortion (vibrations) in the IR and electronic oscillations in the UV-Vis. Note that in between there is no strong coupling: This will define the <u>optical transparency window</u> of the glass.

Lorentz Oscillator:

In the transparency window, the electrons oscillate in response to the E field of light but its motion is damped by collision with other electrons.



Newton's law of dynamic (**ΣF = ma**) for a forced oscillator with damping:

$$m\left(\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \omega_0^2 x\right) = qE$$

where x is the displacement along E, γ is the damping factor, m is the mass of the electron and q its charge.

electrostatic force

acceleration

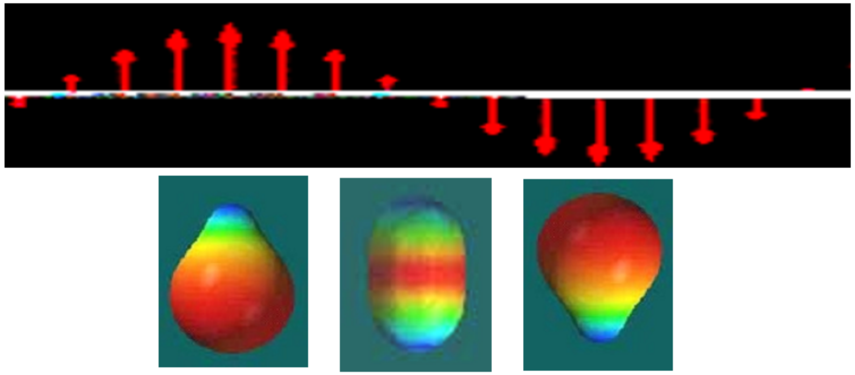
restoring force
(resonance)

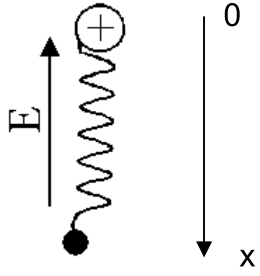
damping

Lorentz Oscillator:

Oscillating E field: $E = E_0 e^{i\omega t}$

Resulting dipole oscillation: $x = x_0 e^{i\omega t}$





Combine $m\left(\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}x}{\mathrm{d}t} + \omega_0^2 x\right) = qE$ and $x = x_0 e^{i\omega t}$ and solve for x.

This gives $x = \frac{q/m}{\omega_0^2 - \omega^2 + i\gamma\omega}E$ the displacement or distortion of the electronic dipole.

And the resulting dipole polarization $p = qx = \frac{q^2/m}{\omega_0^2 - \omega^2 + i\gamma\omega}E$

Lorentz Oscillator:

For N electrons of charge q the total polarization P is: $P = N\frac{q^2/m}{\omega_0^2 - \omega^2 + i\gamma\omega}E$

And for various oscillators N_j with resonant frequency ω_j:

$$P = \underbrace{\left(\frac{q^2}{m}\sum_j \frac{N_j}{\omega_j^2 - \omega^2 + i\gamma_j\omega}\right)}_{} E$$

$$P = \varepsilon_0 \chi E$$

We now have an expression for the polarizability or dielectric susceptibility of the material: χ

$$\chi = \frac{q^2}{\varepsilon_0 m}\sum_j \frac{N_j}{\omega_j^2 - \omega^2 + i\gamma_j\omega}$$

The Refractive Index:

χ is directly related to the refractive index n through the dielectric constant of the materials ε_r according to:

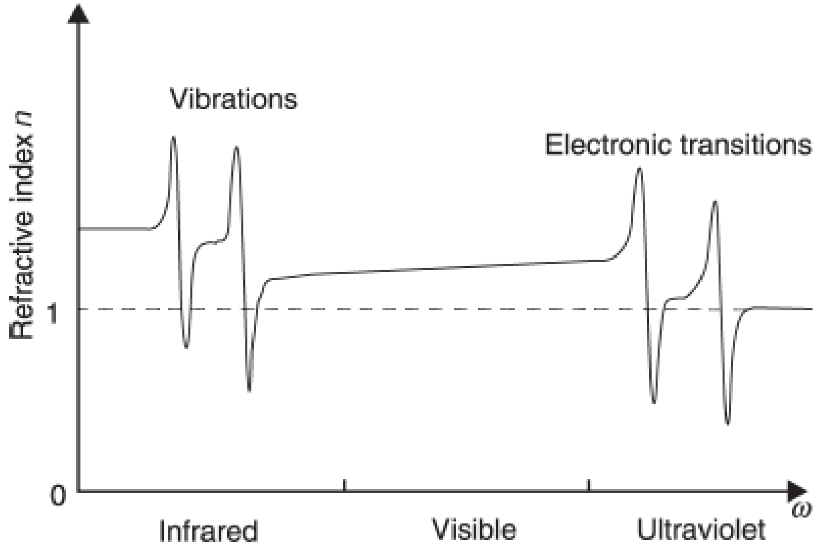
$n = \sqrt{\varepsilon_r}$ and $\varepsilon_r = 1 + \chi$ or $n^2 = 1 + \chi$

We now have an expression for the refractive index of the material as a function of the light frequency ω:

$$n^2 = 1 + \frac{q^2}{\varepsilon_0 m} \sum_j \frac{N_j}{\omega_j^2 - \omega^2 + i\gamma_j \omega}$$

Note that the refractive index is a complex quantity: **n**=n+iκ

Variation of Refractive Index with frequency:



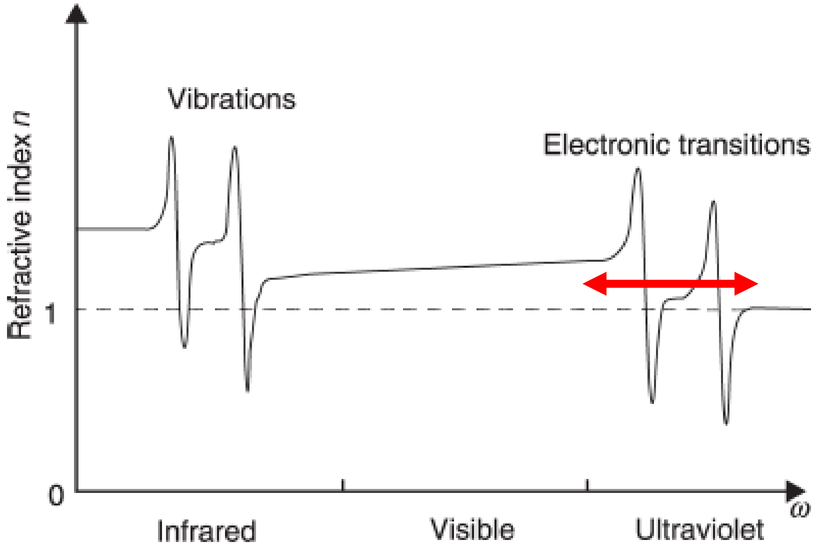
$$n^2 = 1 + \frac{q^2}{\varepsilon_0 m} \sum_i \frac{N_j}{\omega_j^2 - \omega^2 + i\gamma_j \omega}$$

For $\omega < \omega_j$, the term $(-\omega^2 - i\gamma\omega)$ is negligible in comparison to ω_j^2 and n is almost constant between resonances.

However it should be noticed that for increasing ω the denominator slightly decreases and n therefore increases with ω. This is the reason for light dispersion (prism).

For $\omega = \omega_j$, the term $(\omega_j^2 - \omega^2) \rightarrow 0$, the denominator decreases and n shows a resonance peak.

Refractive Index: Resonant region



$$n^2 = 1 + \frac{q^2}{\varepsilon_0 m} \sum_i \frac{N_j}{\omega_j^2 - \omega^2 + i\gamma_i \omega}$$

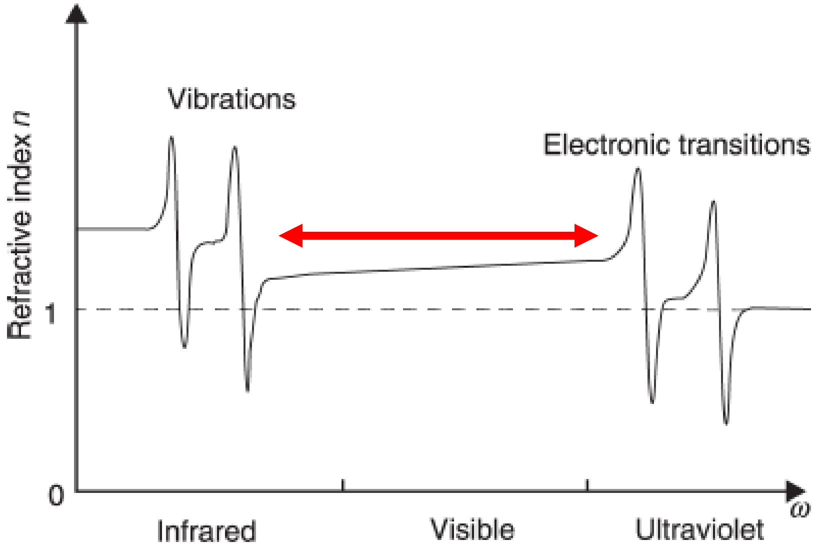
n=n+iκ

At the resonance $\omega = \omega_j$, the term $(\omega_j^2 - \omega^2) \rightarrow 0$, and the index therefore becomes imaginary. **n** is therefore controlled by the extinction coefficient κ.

The damping factor iγω dominate and results in large loss of energy. The resonance is therefore associated with strong attenuation or absorption of the wave.

Indeed: $\alpha = \dfrac{2\kappa\omega}{c}$ where α is the absorption coefficient.

Refractive Index: Transparent region



$$n^2 = 1 + \frac{q^2}{\varepsilon_0 m} \sum_j \frac{N_j}{\omega_j^2 - \omega^2 + i\gamma_j \omega}$$

$\mathbf{n} = n + i\kappa$

In the transparent region, the term $(\omega_j^2 - \omega^2) >> i\gamma\omega$, and the index becomes mostly real.

The damping factor $i\gamma\omega$ is negligible, there is no significant absorption and the material is transparent.

We normally approximate that $\mathbf{n} = n$ in the transparency region. That is why refractive indices are listed as real quantities in optics tables.

QUESTIONS?

BIBLIOGRAPHY:

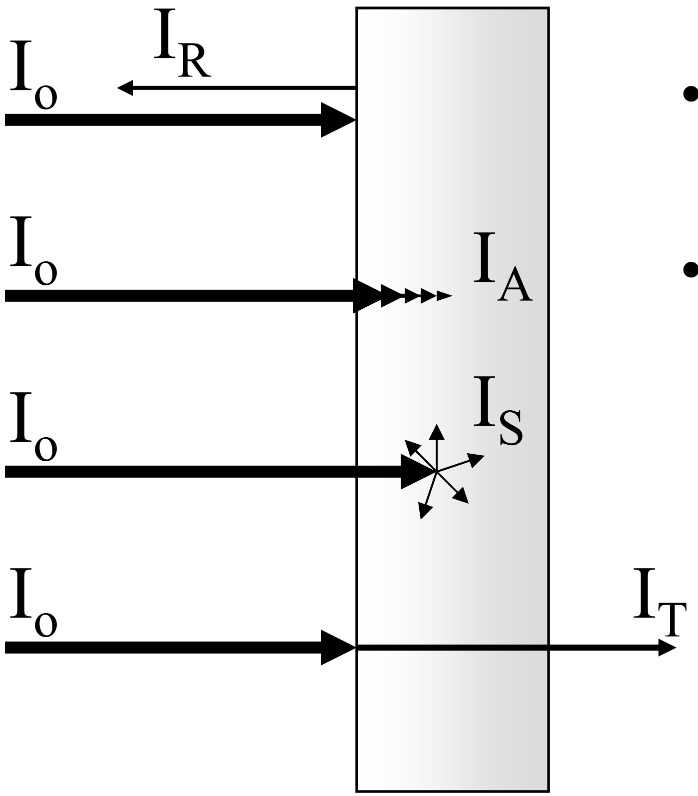
For a detailed recap of these topics, see:

P. Lucas, Measurement of Optical Properties of Solids, *Encyclopedia of Modern Optics*, edited by Robert D. Guenther, Duncan G. Steel and Leopold Bayvel, Elsevier, Oxford, (2004)

The pdf of this chapter is posted on the Glass Course web site (available for download).

Measurement of optical parameters

- Four things can happen when light proceeds into a solid.



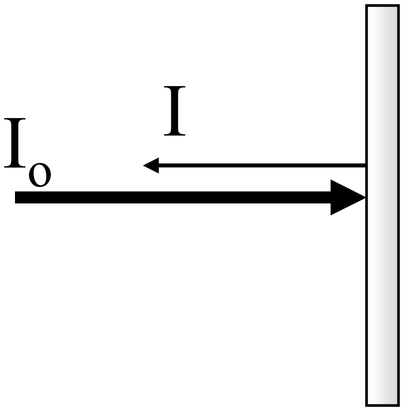
- Part of the light can be reflected by the surface of the solid. Reflection
- Part of the light can be absorbed by coupling into the solid. Absorption
- Part of the light can be scattered by the atoms and defects in the solid. Scattering
- Part of the light can be transmitted through the solid. Transmission

- Therefore, for an incident beam of intensity I_o entering the solid:

$$\mathbf{I_o = I_R + I_T + I_A + I_S}$$

Measurement of optical parameters: Reflection

The intensity reflected at the surface of a glass is determined by the reflectance R defined for a incident beam normal to the surface according to the Fresnel equation:



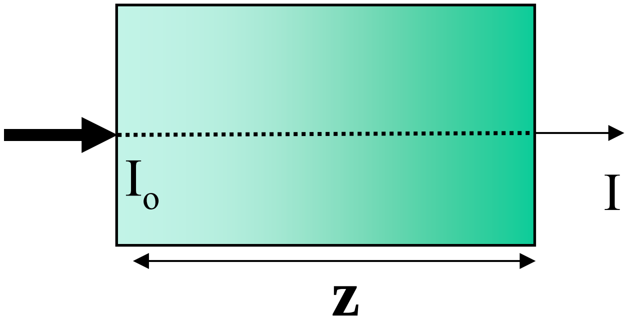
$$R = \frac{I}{I_0} = \frac{(n-1)^2+\kappa^2}{(n+1)^2+\kappa^2}$$

For measurements performed in the transparency region κ=0 and $R = \left(\frac{n-1}{n+1}\right)^2$

This provides us with a formula relating a measurable quantity (R) to the optical constant of the material n.

Measurement of optical parameters: Absorption

In the resonant regions the phenomenon of absorption correspond to transfer of energy from the light wave into the material.



$$\frac{I}{I_o} = e^{-\alpha z}$$

The intensity of the wave decays exponentially with path length z according to Beer’s law:

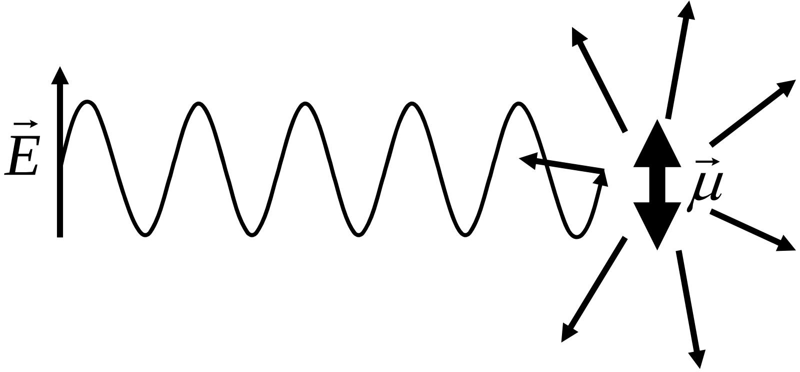
$I \propto e^{-\frac{2\omega\kappa z}{c}}$ or $I \propto e^{-\alpha z}$ where α is the absorption coefficient

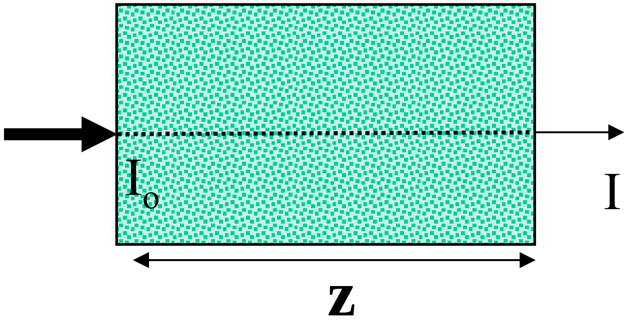
This provides us with another formula relating a measurable quantity (α) to the imaginary part κ of the optical constant of the material.

$$\alpha = \frac{2\kappa\omega}{c}$$

Measurement of optical parameters: Scattering

Rayleigh Scattering results from microscopic density fluctuations and corresponds to redirecting light in multiple directions. No energy is transferred to the material during Rayleigh scattering. (**Elastic scattering** unlike Raman scattering)



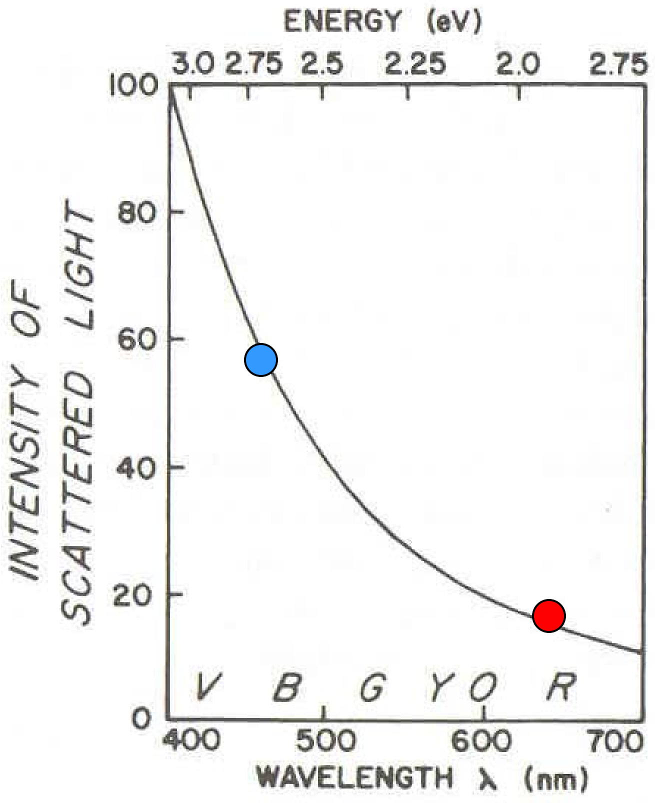


The intensity of the wave decays exponentially with path length z in a way analogous to Beer’s law:

$$I(z) = I_0 e^{-Sz} \quad \text{and} \quad S(\lambda) \propto \frac{1}{\lambda^4}$$

Measurement of optical parameters: Scattering

- The shorter the wavelength, the higher the scattering efficiency.



$$I_S = \frac{a}{\lambda^4} I_o$$

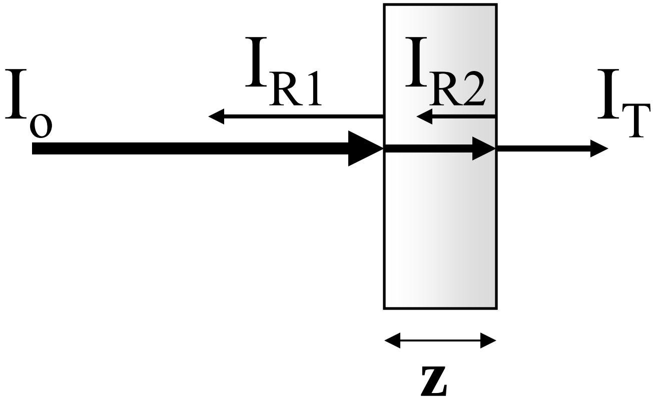
- The scattering intensity decreases with λ^4.

- For example, blue light is scattered much more efficiently than red light

Measurement of optical parameters: Transmission

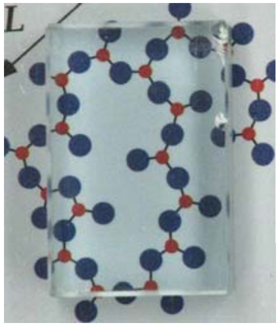
Glasses are homogeneous material and scattering is usually negligible. If we disregard scattering then R+T+A=1.

The transmission through a slab of glass must then account for absorption as well as reflection on front and back surface.



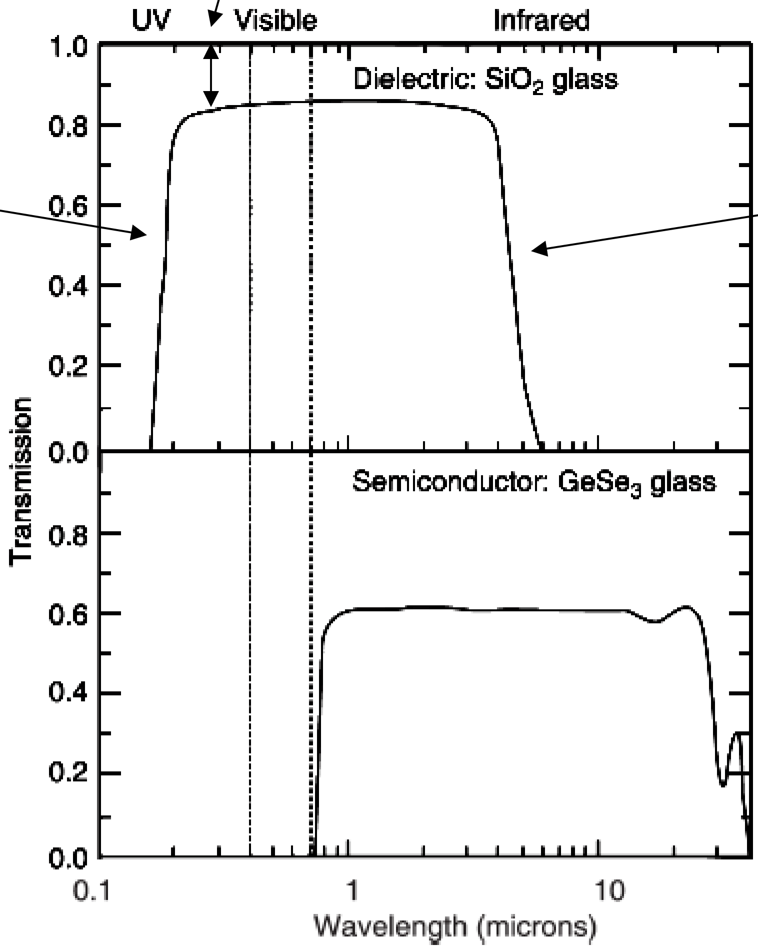
The expression for the transmittance is then: $T = \frac{I_T}{I_0} = (1-R)^2 e^{-\alpha z}$

Optical window



Reflection

Electronic transitions



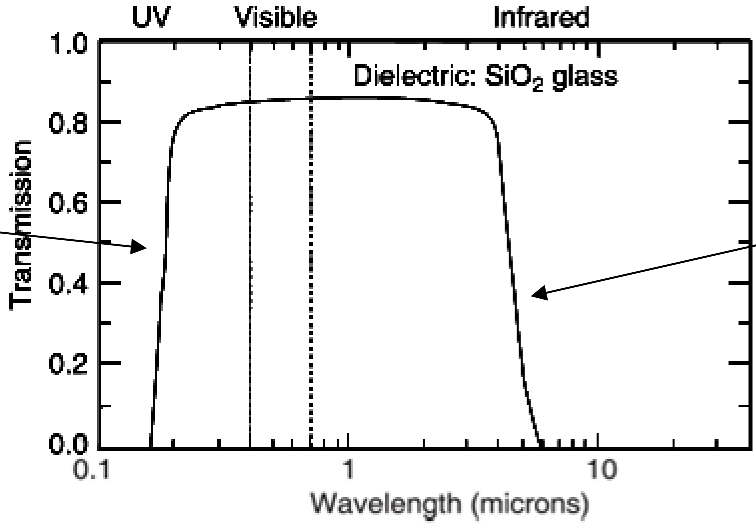
Multiphonon vibrations

Spectrometers:

- No spectrometer has light sources and detectors that cover the entire range of wavelength, we need two types of spectrometers to fully characterize a glass optical window.

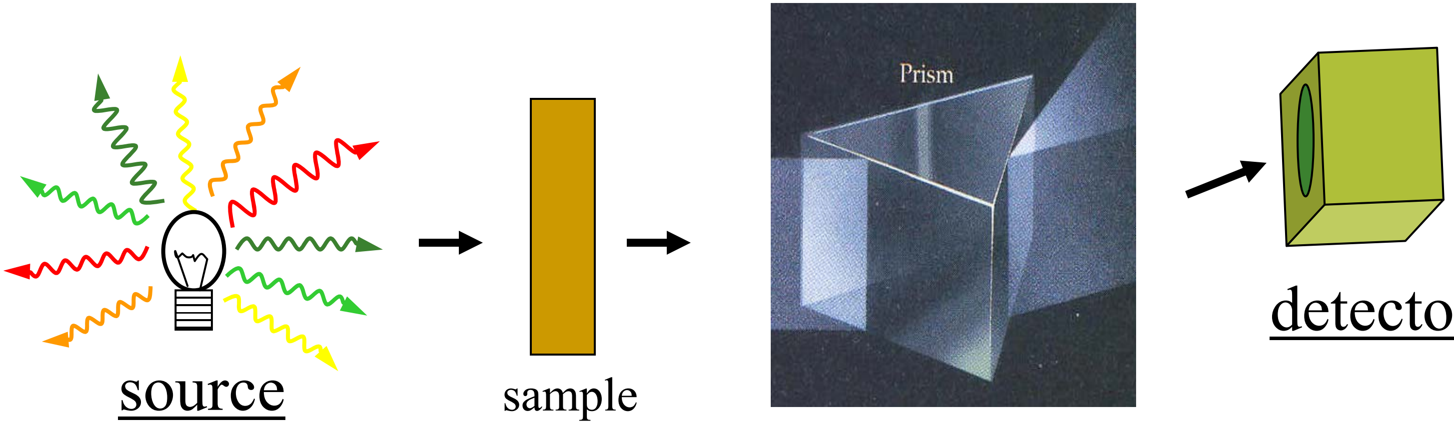
Infrared spectrometer

UV-visible spectrometer



Spectrometers:

- Most spectrometer consist of three parts:
    - A light source covering the range of interest (infrared, UV etc..)
    - A monochromator to discriminate wavelengths
    - A detector to measure the transmitted intensity through the sample

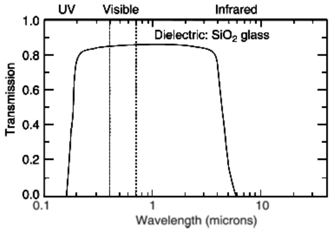


source

sample

monochromator

detector



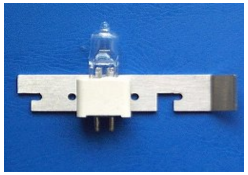
UV- Vis - NIR Spectrometers:

- Typically covers a range of wavelength from 180 nm to 3000 nm which include UV, visible and near infrared.

LIGHT SOURCE

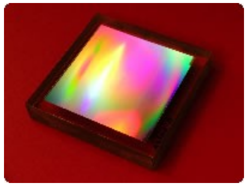
Deuterium lamp are used as light source for the **UV** range.

Tungsten or halogen lamps are used for the **visible** region.



MONOCHROMATOR

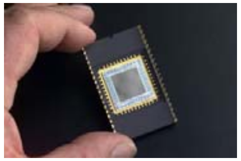
Gratings are more efficient, smaller and cheaper than prism.



DETECTOR

Photomultipliers tube (PMT):

Charge Coupled Device (CCD):



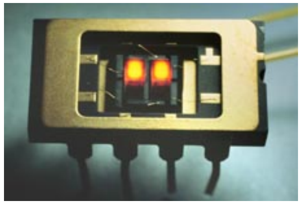
Silicon semiconductor

FTIR Spectrometers:

- Typically covers the wavelength range from 2 μm (2000 nm) to 30 μm which includes all molecular vibrations

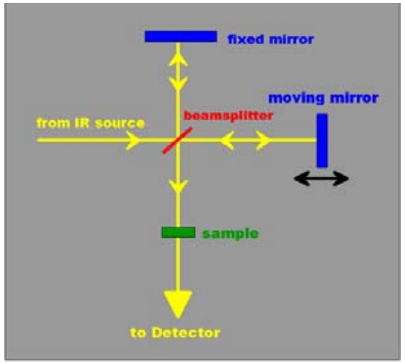
LIGHT SOURCE

Glow bar: Black body Radiations (heated coil of **silicon carbide**)



INTERFEROMETER

(Not technically a MONOCHROMATOR)



DETECTOR

Pyroelectric Detectors

MCT (HgCdTe)

highly sensitive for low intensity