Advanced Vitreous State – The Physical Properties of Glass

Passive Optical Properties of Glass

Lecture 2:

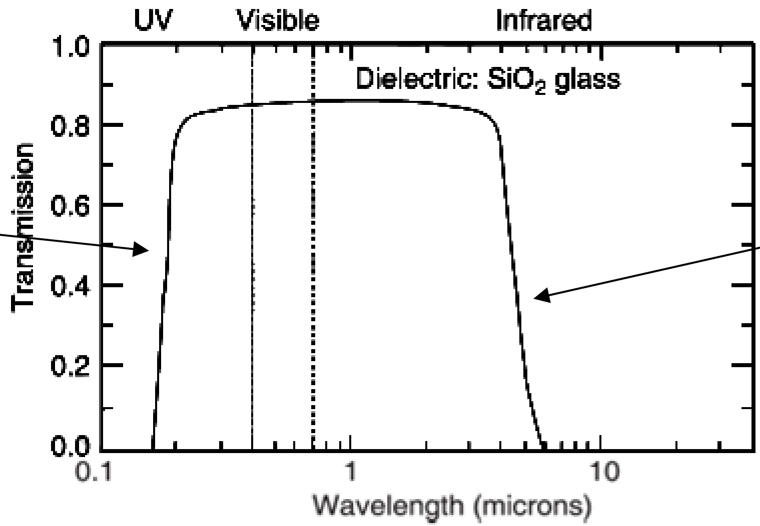
Pierre Lucas
Department of Materials Science & Engineering
University of Arizona
Tucson AZ
Pierre@u.arizona.edu

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.

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

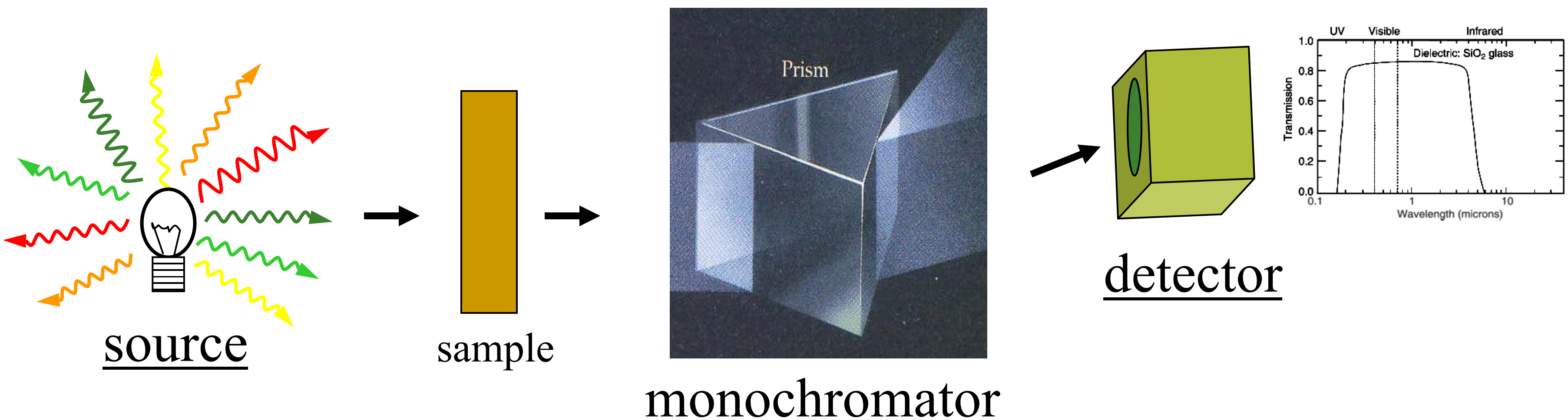
UV-visible spectrometer



Infrared 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



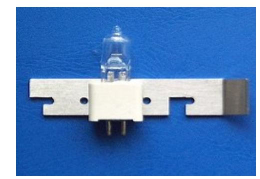
UV- Vis - NIR Spectrometers:

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

LIGHT SOURCE

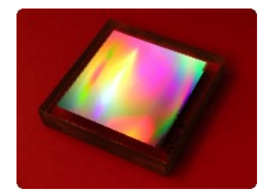
Deuterium lamp are used as light source for the **UV** range.

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



MONOCHROMATOR

Gratings are more efficient, smaller and cheaper than prism.

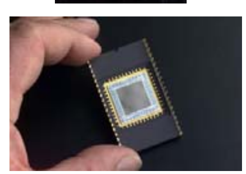


DETECTOR UV-Vis(180-860nm)

Photomultipliers tube (PMT):

Charge Coupled Device (CCD):

Silicon semiconductor



DETECTOR NIR (860-3000nm)

InGaAs: 860-2000nm

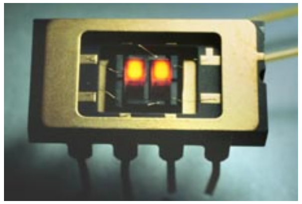
PbS: 2000-3000nm

FTIR Spectrometers:

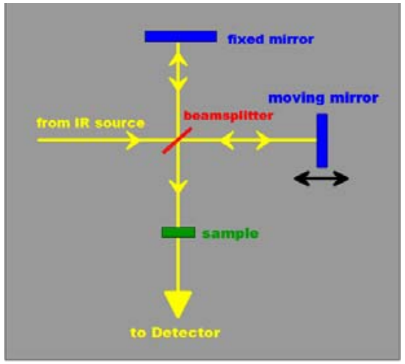
•Typically covers the wavelength range from 2 μm (2000 nm) to 30 μm which includes all molecular vibrations

LIGHT SOURCE

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



INTERFEROMETER



Journal of Chemical Education **63,** A5, A269, A296 (1986)

(Not technically a MONOCHROMATOR)

DETECTOR

Pyroelectric Detectors

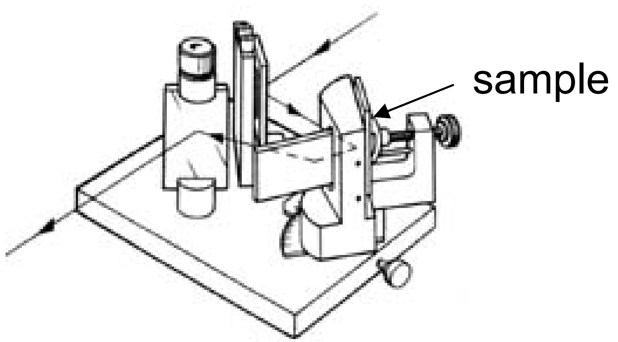
MCT (HgCdTe)

highly sensitive for low intensity

Reflection spectroscopy.

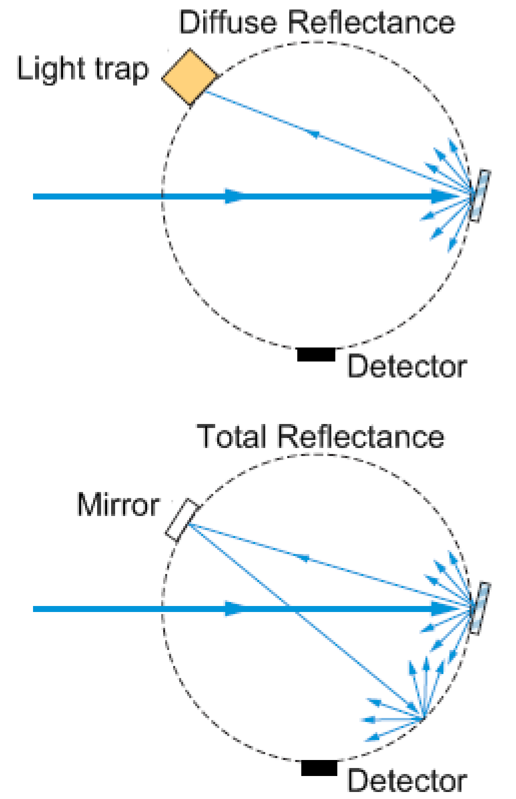
$$R = \left(\frac{n-1}{n+1}\right)^2$$ for normal incident beam only

Specular Reflection stage



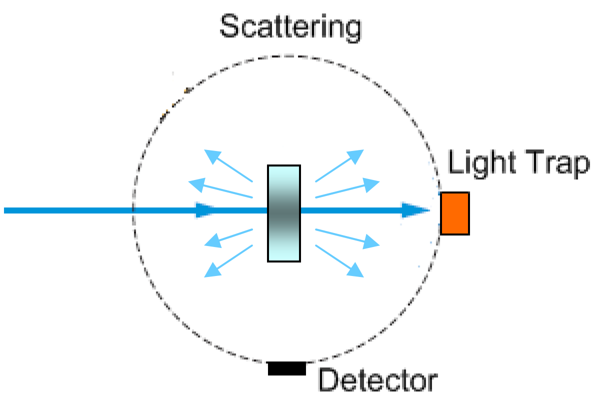
Measurement at variable angle

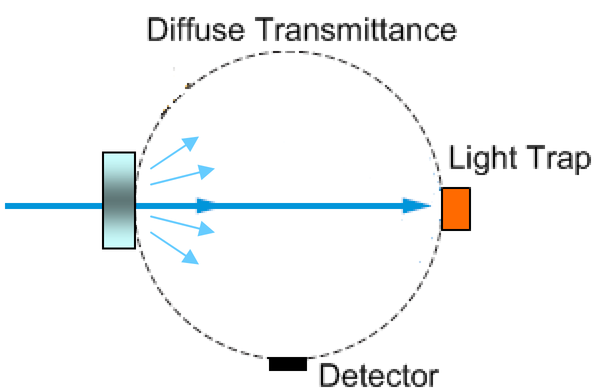
Diffuse Reflection Integrating Sphere



Important in glass window industry to assess solar reflectance of glass and coatings

Scattering:





Scattering intensity at variable wavelength can be estimated using an integrating sphere detector.

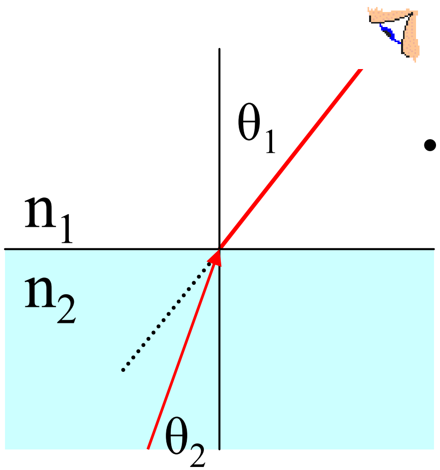
Complementary measurements of transmittance, diffuse transmittance, reflection and scattering allow to extract the contribution of each effects.

Refraction

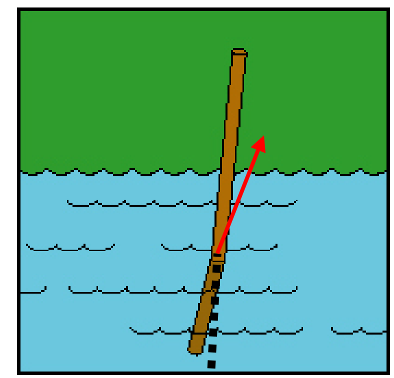
When light propagates into a material, it polarizes the medium: $n = \sqrt{\varepsilon}$

This interaction slows down the light to a velocity v < c according to: $n = \dfrac{c}{v}$

- A consequence of that change in velocity is **refraction** which bends a light ray as it proceeds into a medium of different refractive index.



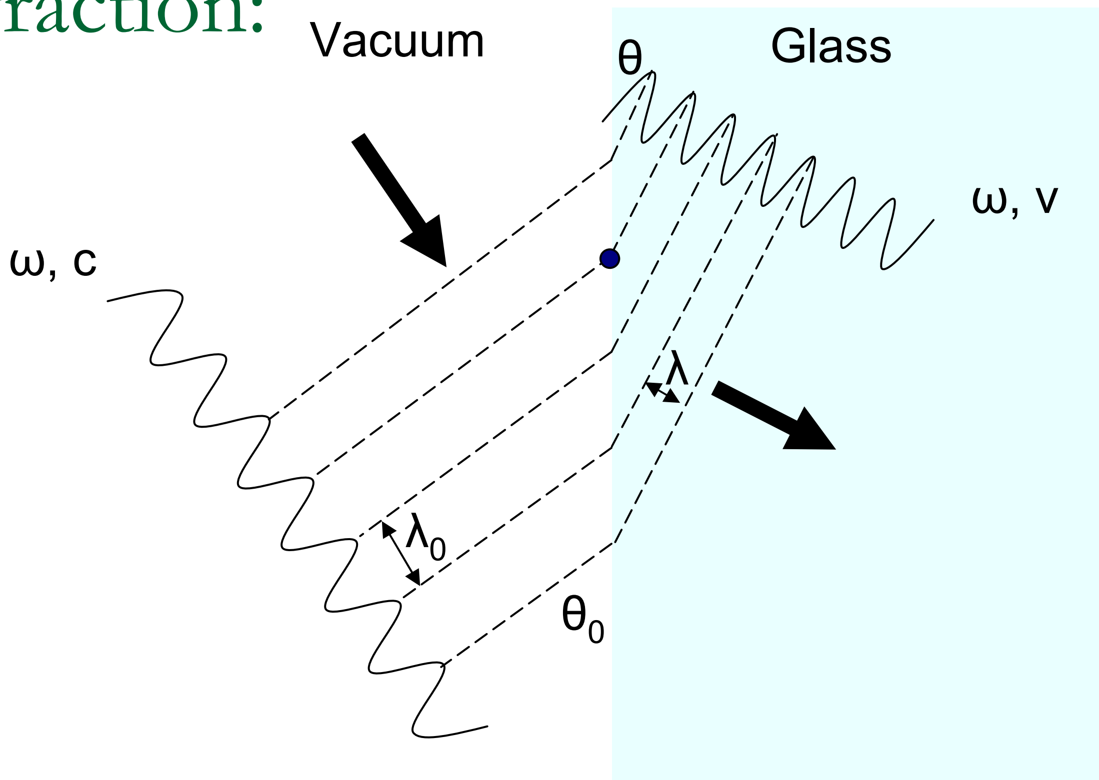
- A well known consequence of refraction is the distorted aspect of a stick immersed in water.



- The angle of refraction depends on the difference in refractive index between the two mediums according to Snell's law:

$$\sin\theta_1 = \frac{n_2}{n_1}\sin\theta_2$$

Refraction:



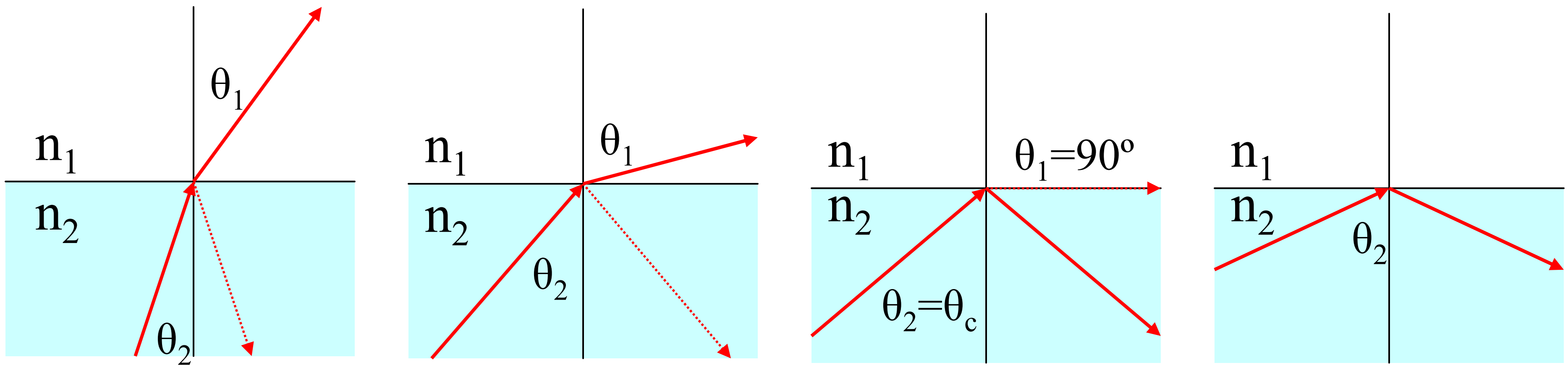
A charge sitting at the interface must feel only one frequency (ω).
However the wave propagating in the glass has a lower velocity v<c.
This means the distance between two crest (λ) must be shorter.

$$\lambda_0 = \frac{2\pi c}{\omega} \quad and \quad \lambda = \frac{2\pi v}{\omega}$$

The only way to achieve this is for the wave to travel at a different angle.

Total internal reflection

- According to the relationship $\sin\theta_1 = \frac{n_2}{n_1}\sin\theta_2$ if $n_2 > n_1$ then $\theta_1 > \theta_2$
- And as θ_2 becomes larger, θ_1 gradually approaches tangency with the boundary.

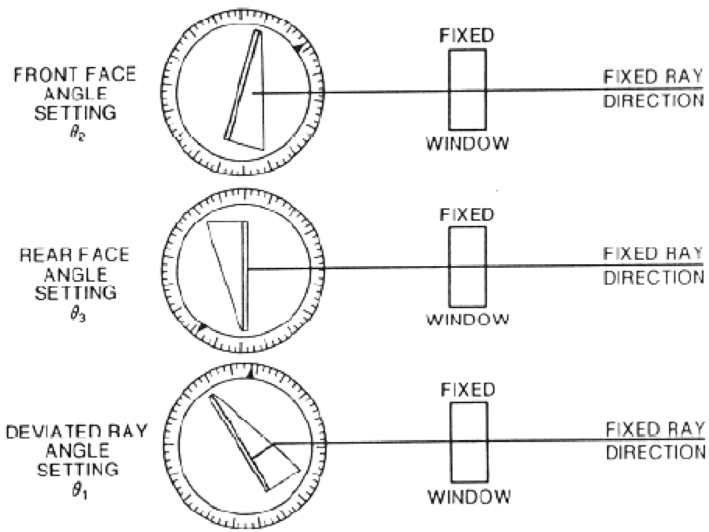


- At the critical angle θ_c the refracted beam reach the surface and θ_1=90º
- The value of the critical angle is given by $\sin\theta_c = \frac{n_1}{n_2}$
- For all angle angle θ_2 larger than the critical angle θ_c all the light is reflected back into the incident medium. This process is known as **total internal reflection**.

Refractive Index measurement

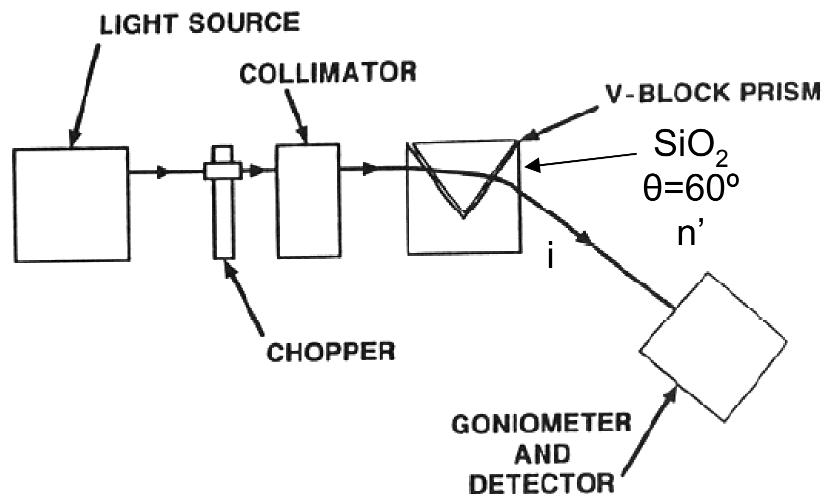
Refraction angle measurements are the method of choice for accurate determination of refractive index n.

Prism Autocollimation



$$n = \frac{\sin(\theta_2 - \theta_1)}{\sin(\pi - (\theta_3 - \theta_3))}$$

V-Block



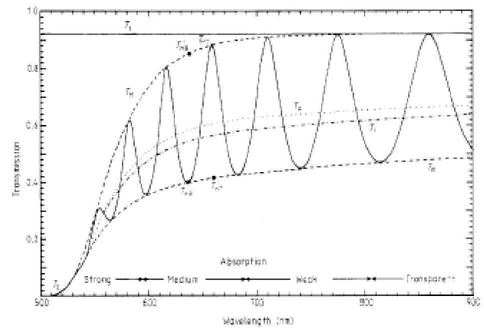
$$n = \sqrt{\tfrac{1}{3}[2\sin^2 i + \sqrt{3}n'\sin i + 2n'^2 + (2\sqrt{3}\sin i + n')\sqrt{n'^2 - \sin^2 i}\,]}$$

J.W. Fleming, Experimental Techniques of Glass Science, American Ceramic Society (1993)

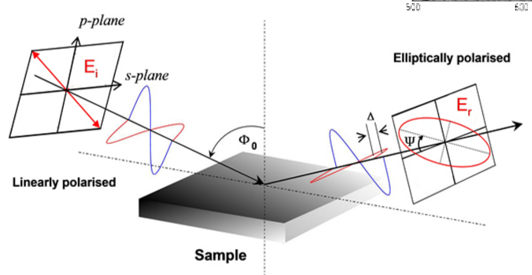
Refractive Index measurement

Standard techniques for index characterization in film:

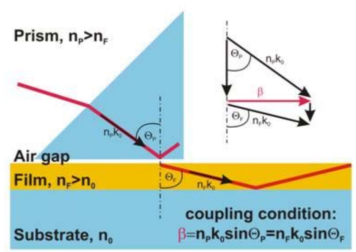
- Transmission/Reflection:



- Ellipsometry:



- Prism Coupling:

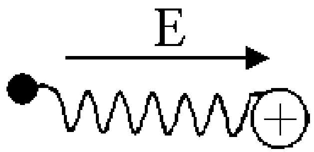


QUESTIONS?

BIBLIOGRAPHY:

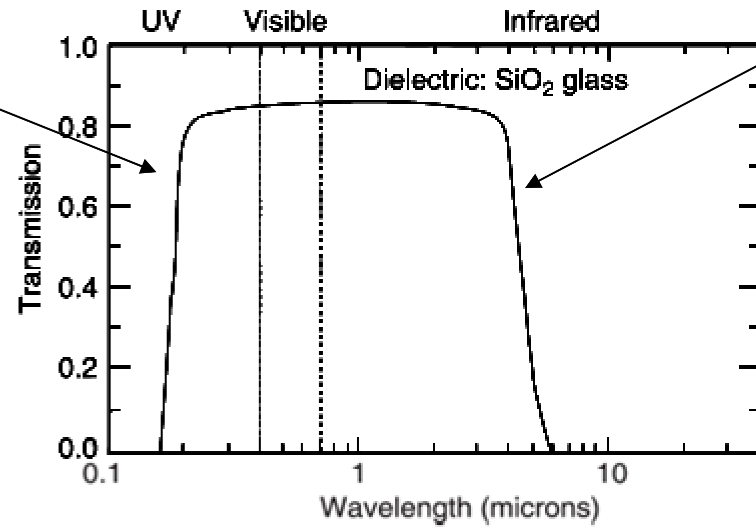
Experimental Techniques of Glass Science, Edited by C. J. Simmons and O. H. El-Bayoumi, American Ceramic Society (1993)

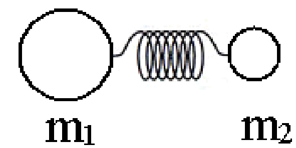
Optical Window of Glasses:



$$\omega_0 \propto \sqrt{\frac{1}{\mu}}$$

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$



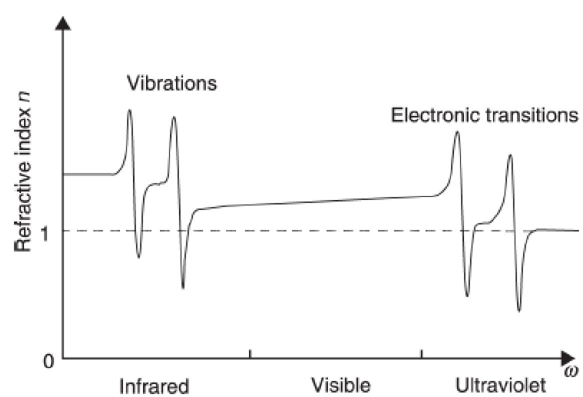


$$\omega_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

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

Lorentz Oscillators

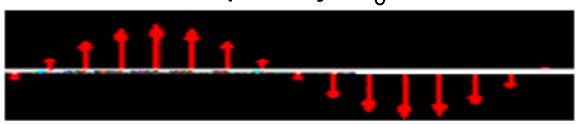


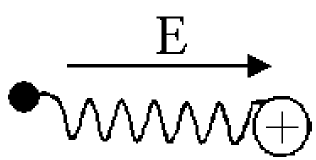
Correlation between Quantum and Classic models

Classic:

light=wave
electron=particle

frequency ω_0





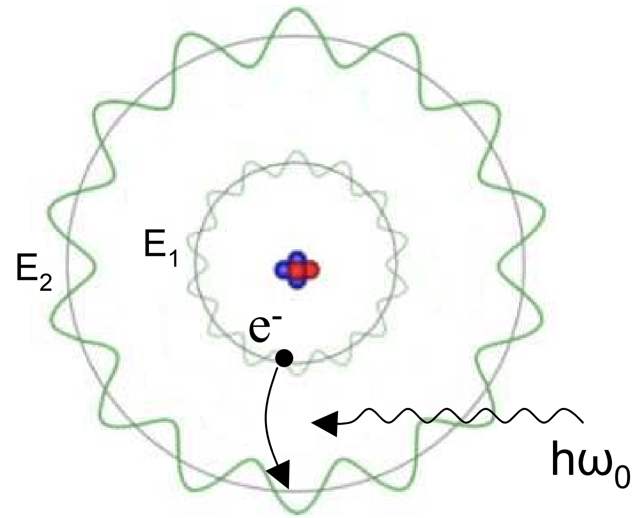
$$\omega_0 \propto \sqrt{\frac{1}{\mu}} \qquad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

Absorption occurs when light wave frequency ω_0 is equal to the resonant frequency of oscillator

Quantum:

light=photon
electron=wave

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$



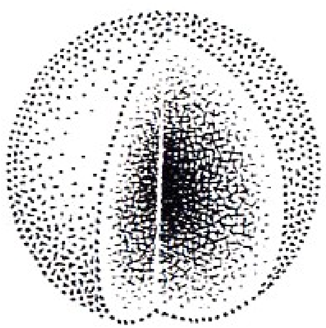
Absorption occurs when photon energy $h\omega_0$ is equal to the difference between electronic levels $\Delta E = E_2 - E_1$

Quantum Description of Electrons in Solids

Electrons behave as standing wave and are described by wavefunctions ψ which are solutions to the Schrodinger equation.

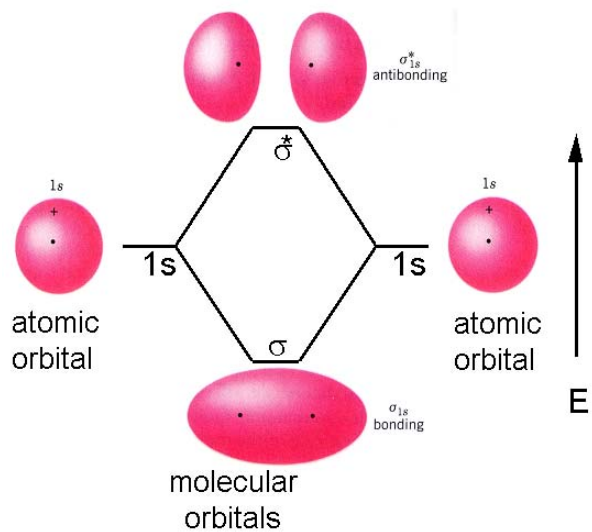
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Atom

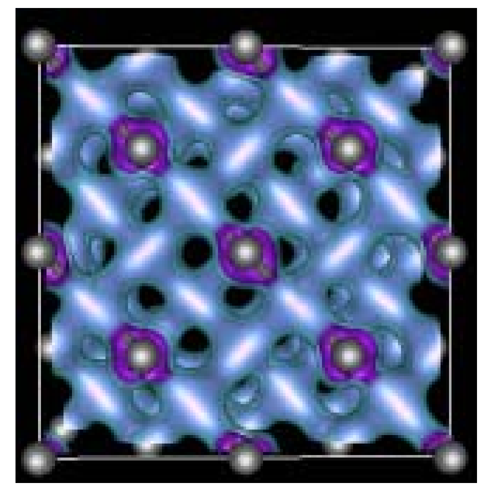


$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_o}\right)^{3/2} e^{-zr/a_o}$$

Molecule



Solid

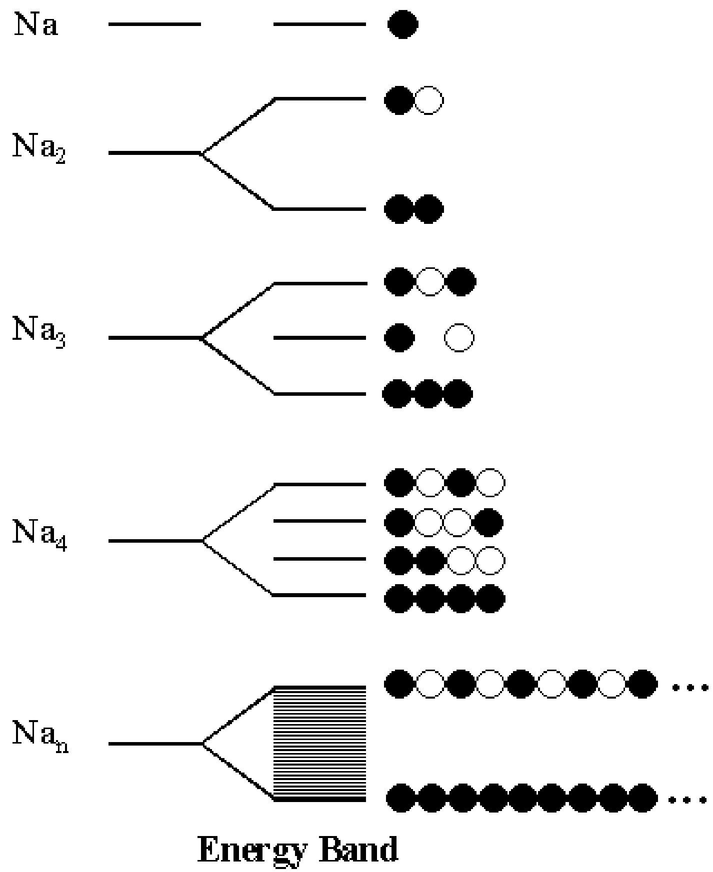


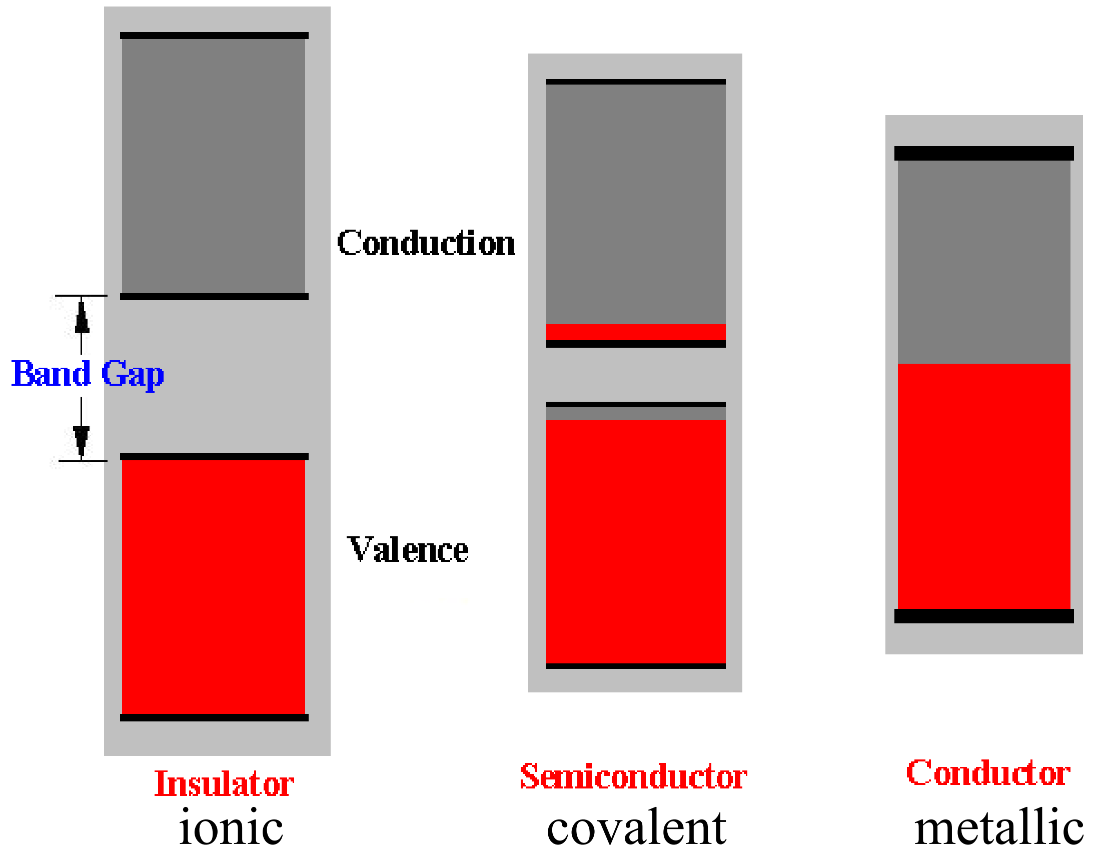
$$\Psi(r) \propto e^{ik.r} U(r)$$

Bloch function

Electronic Band Structure

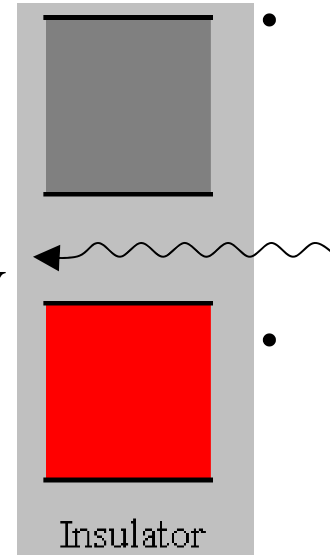
- On the short wavelength side, light absorption is due to electronic transitions across energy levels in the band structure.





Transparent solids:

NaCl E_g=8.5 eV

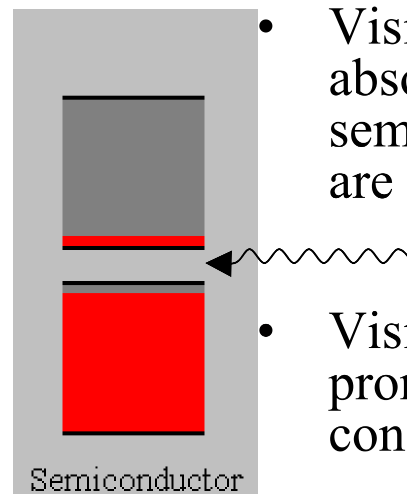


- Visible light is not absorbed by insulator: they are transparent

$h\upsilon$ not absorbed

- Visible photons are not energetic enough for the band gap

Si E_g=1.1 eV



- Visible light is absorbed by semiconductors they are opaque

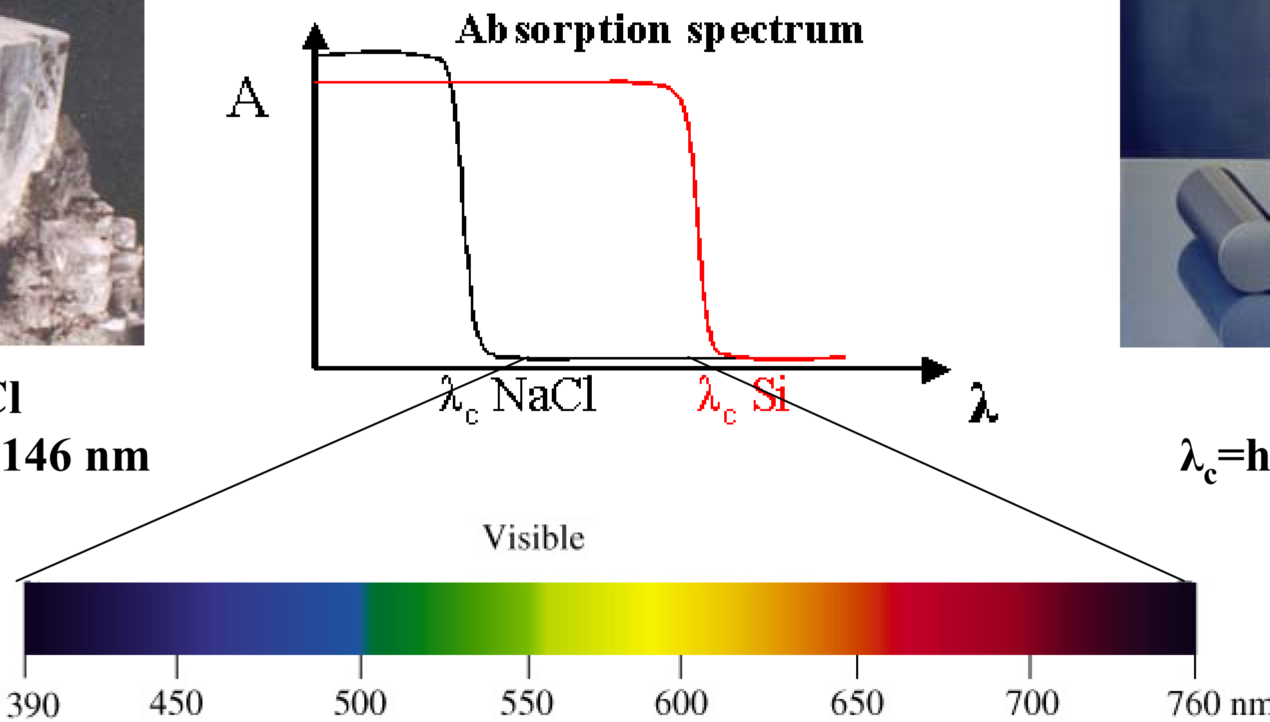
$h\upsilon$ absorbed

- Visible photon can promote an e^- in the conduction band.

Transparent solids:

- A solid with bandgap E_g has a cut off wavelength define as $\boldsymbol{\lambda_c = hc/E_g}$.
- The solid will absorb photons of wavelength shorter than λ_c (higher energy photons) and be transparent for photons with wavelength longer than λ_c (lower energy photon).

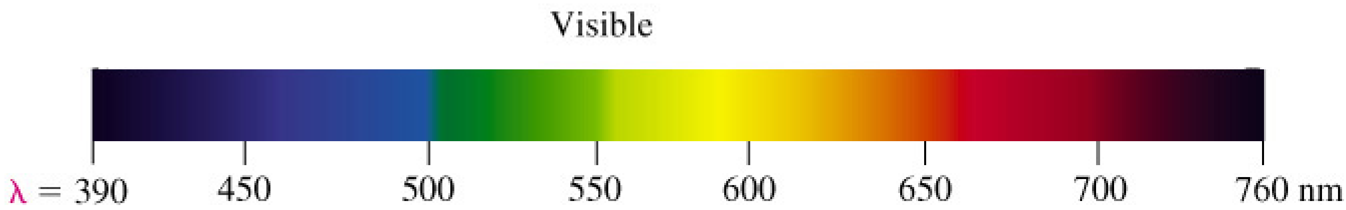
NaCl
$\boldsymbol{\lambda_c = hc/E_g = 146}$ **nm**

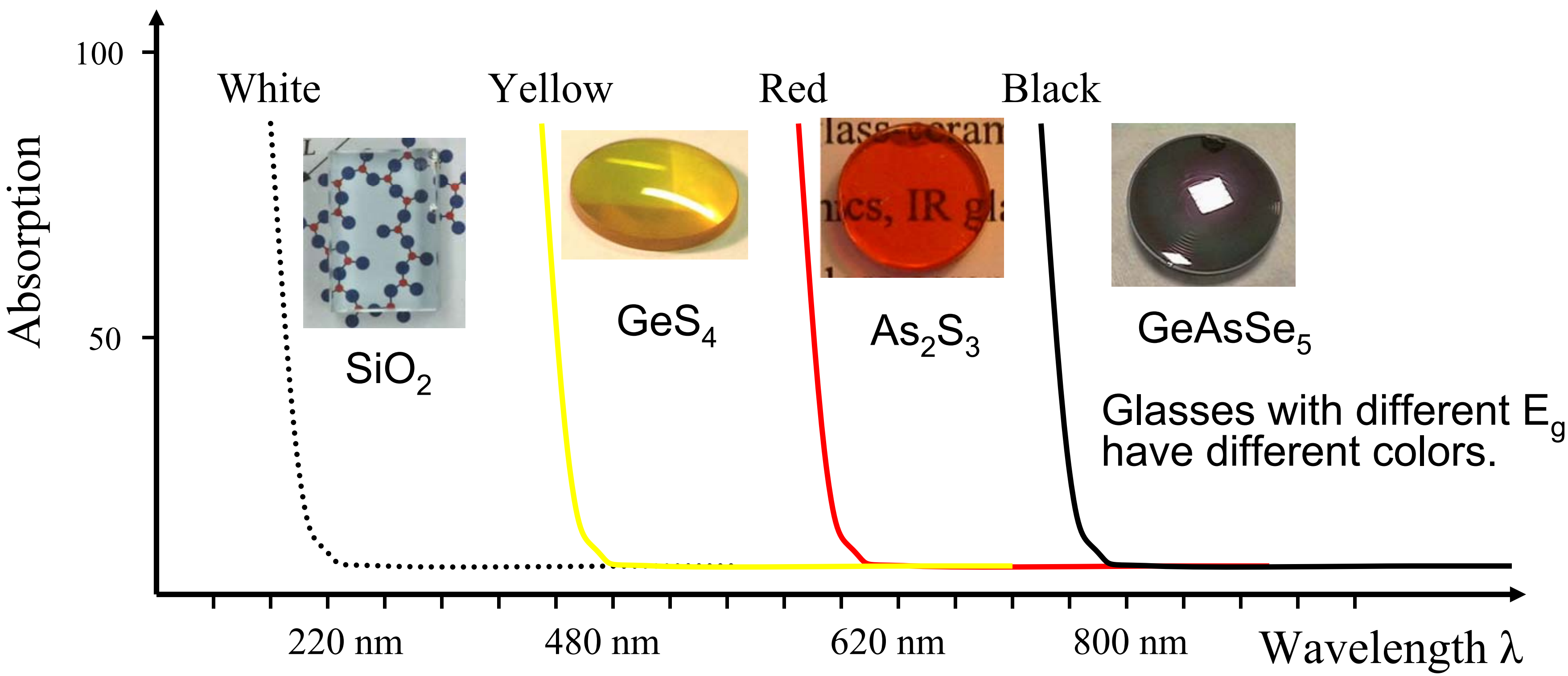


Si
$\boldsymbol{\lambda_c = hc/E_g = 1130}$ **nm**

Optical window of transparent materials

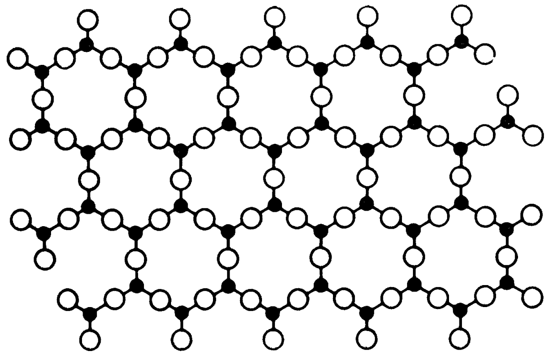
- Due to bandgap absorption, solids filter out all the visible light with wavelength shorter than λ_c and appear colored.

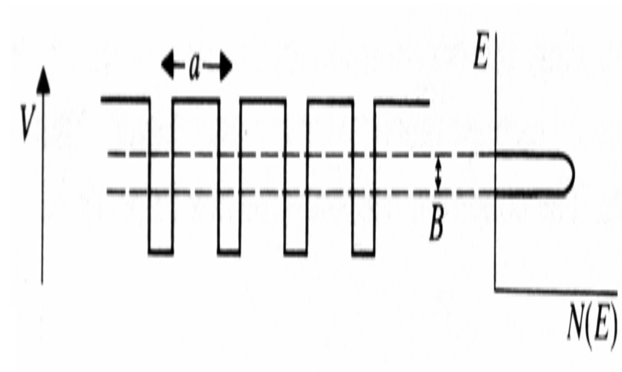




Band edge in glass

CRYSTAL



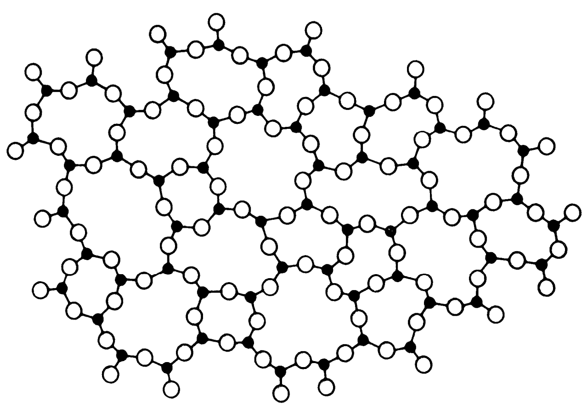


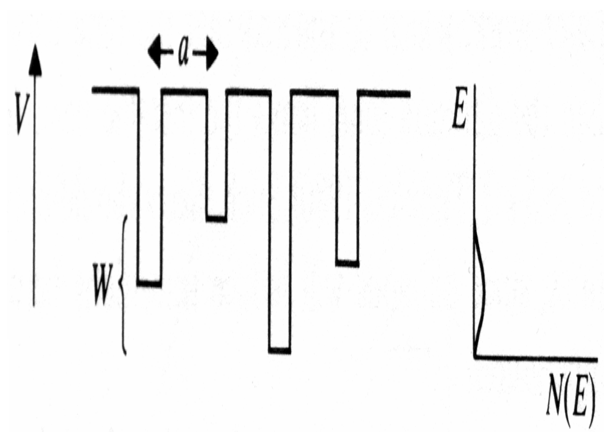
Bloch function

$$\Psi(r) \propto e^{ik.r} U(r)$$

- *Electrons: delocalized.*
- *Density of state: sharp band.*

GLASS





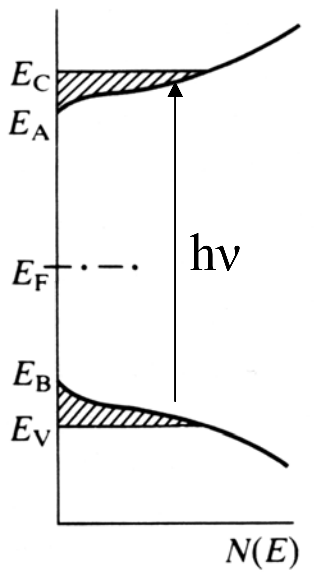
α_L: Localization Length

$\alpha_L \propto (\xi_o - \xi)$

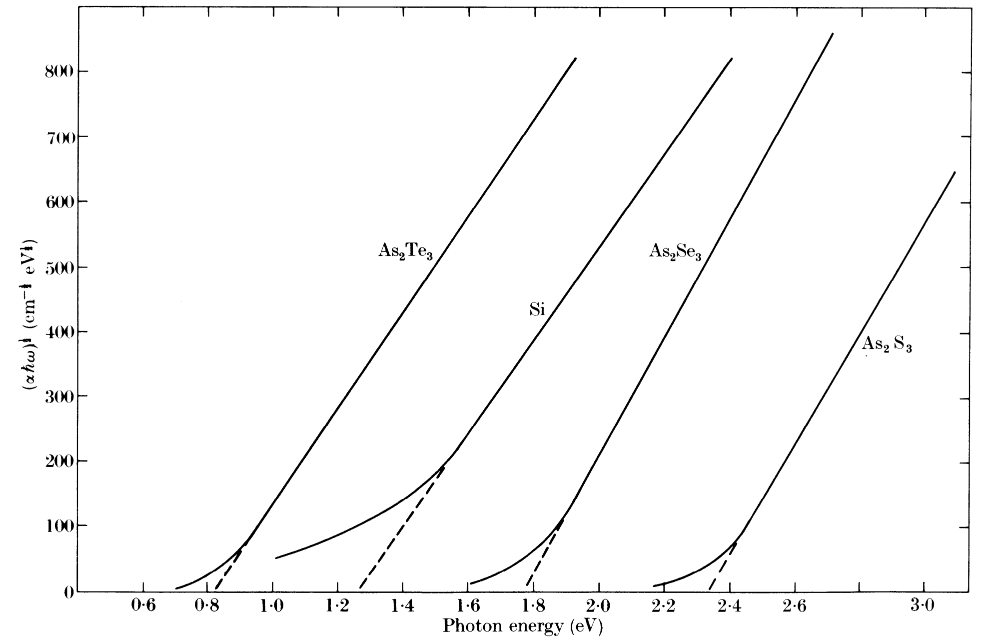
$$\Psi(r) \propto \exp(-\alpha_L r)$$

- *Electrons: localized at the top of band.*
- *Density of state: spread out.*

Band edge in glass



BANDING TAILING IN THE DENSITY OF STATE

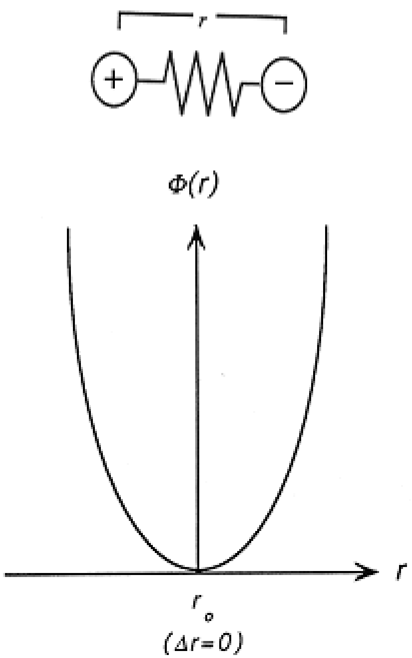


OPTICAL ABSORPTION EDGES OF AMORPHOUS SEMICONDUCTORS

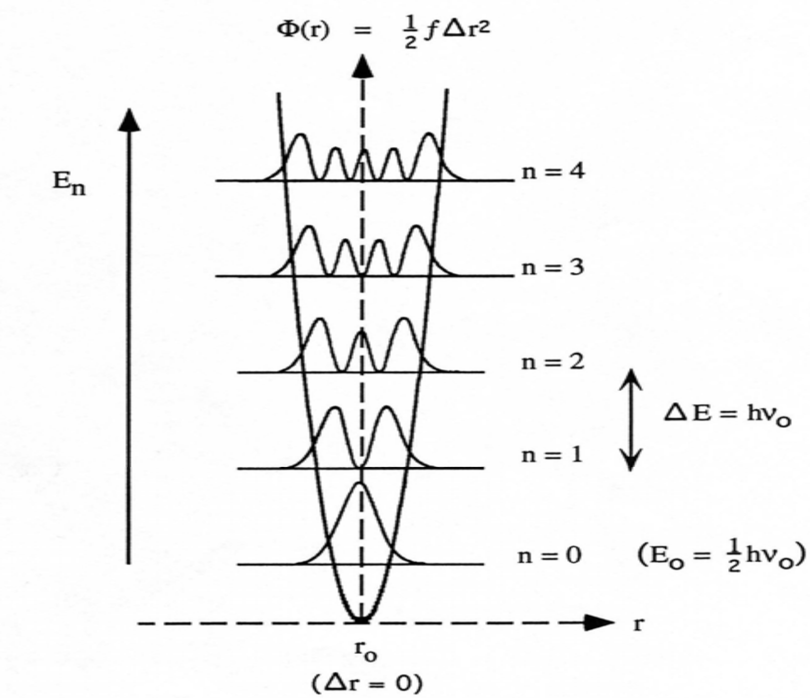
It is the localized states in the sub-bandgap region which are excited during photoinduced processes.

Classical and Quantum model of vibrations:

- CLASSICAL



- QUANTUM



- From equation of motion:

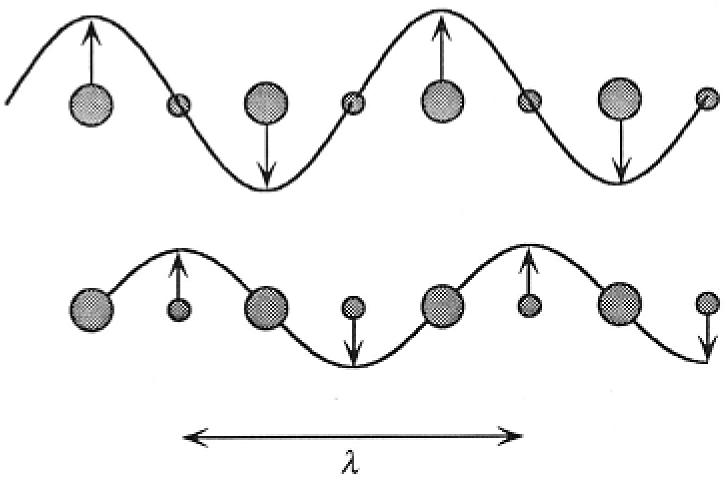
$$\bar{\upsilon} = \frac{1}{2\pi}\sqrt{k\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}$$

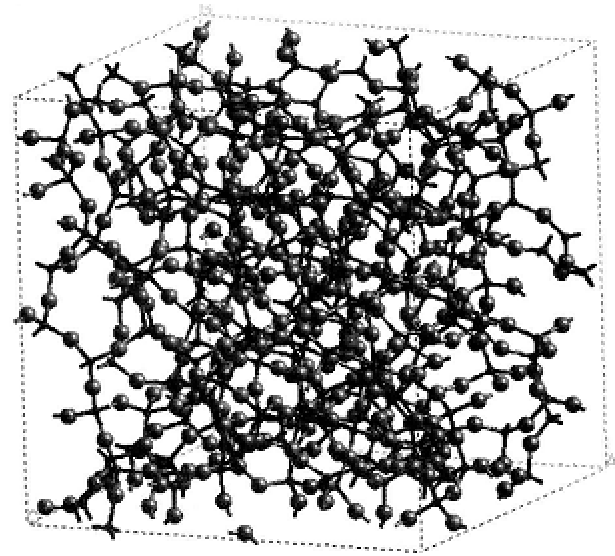
- From Schrodinger's wave equation:

$$E_n = (n+\frac{1}{2})\frac{h}{2\pi}\sqrt{k\left(\frac{1}{m_1}+\frac{1}{m_2}\right)} = (n+\frac{1}{2})h\upsilon$$

Multiphonon vibrations:

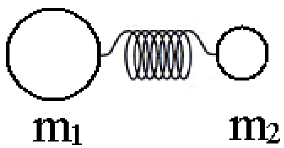
- In solids, many atoms vibrate cooperatively in response to the electric field.





- Due to the large number of atoms there are many many types of vibrational modes, and the solids can absorb infrared light over a wide range of energies (wavelength)

Multiphonon edge in glass:



$$\omega_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$