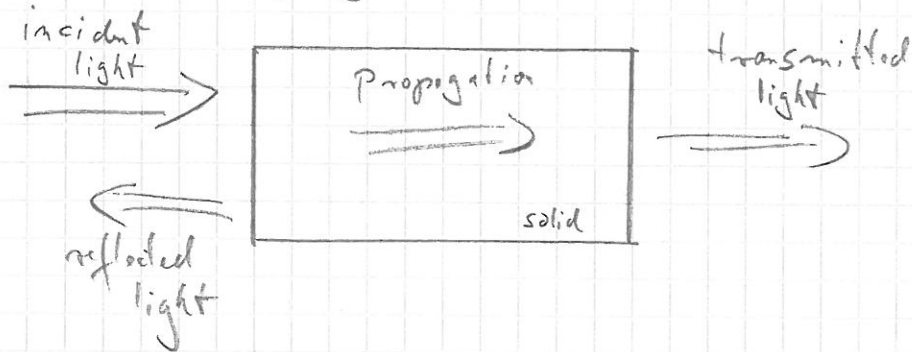


# Optical spectroscopy

The general phenomena that occur when light is shining on a solid can be grouped in reflection, propagation, and transmission:



During propagation, light can be reflected, absorbed, or scattered. Let us now describe these effects mathematically using the respective optical coefficients.

The reflection at surfaces is described by the coefficient of reflection or reflectivity  $R$ .  $R$  is defined as the ratio of reflected power to the power incident on the surface. The coefficient of transmission or transmissivity  $T$  is defined analogously as the ratio of transmitted power to incident power. If there is no absorption or scattering, then by conservation of energy we must have that:

$$R + T = 1$$

The propagation of light through a transparent medium is described by the refractive index  $n$ . It is defined as the ratio of the velocity of light in free space

$c$  to the velocity of light in medium  $v$  according to:  $n = \frac{c}{v}$

In general,  $n$  depends on the wave length. When only a single number for  $n$  is given, this is an approximation for a limited range of wave lengths (e.g., the visible range). The absorption of light is quantified by the absorption coefficient  $\alpha$ . This is defined as the fraction of the power absorbed in a unit length of the medium, which can be expressed in Beer's law (that we have encountered several times so far):

$$I(z) = I_0 e^{-\alpha z}$$

The absorption coefficient is a strong function of frequency so that optical materials may absorb one color but not another.

In a similar way, scattering is described by the scattering cross section  $\sigma_s$ . Together with the number density of scatterers  $N$  this leads to:

$$I(z) = I_0 e^{-N\sigma_s z}$$

Absorption and refraction can also conveniently be described by a single quantity, the complex refractive index  $\tilde{n}$ . It is defined as  $\tilde{n} = n + ik$ , where  $n$  is the normal refractive index and  $k$  is called the extinction coefficient (which is directly related to  $\alpha$ ).

Let us now consider the propagation of an electromagnetic wave through a medium with complex refractive index. For a plane wave travelling in  $z$  direction, the spatial and time dependence of the electric field is given by:

$$E(z, t) = E_0 e^{i(kz - \omega t)}$$

where  $k$  is the wave vector of the light and  $\omega$  is the angular frequency.  $E_0$  is the amplitude at  $z=0$ . In a non-absorbing medium with refractive index  $n$ , the wavelength of the light is reduced by this factor  $n$  compared to the free-space wavelength  $\lambda$ .

Therefore, we have

$$k = \frac{2\pi}{\lambda/n} = n \cdot \frac{2\pi}{\lambda} = n \cdot 2\pi \cdot \frac{\nu}{c} = \frac{n \cdot \omega}{c}$$

This can be generalized to the case of an absorbing medium by allowing the refractive index to be complex:

$$k = \tilde{n} \frac{\omega}{c} = (n + iK) \frac{\omega}{c}$$

Putting this in the equation for the electric field leads to:

$$\begin{aligned} E(z, t) &= E_0 e^{i(kz - \omega t)} \\ &= E_0 e^{i\left(\frac{\omega \tilde{n} z}{c} - \omega t\right)} \\ &= E_0 e^{-\frac{K\omega z}{c}} e^{i\left(\frac{\omega n z}{c} - \omega t\right)} \end{aligned}$$

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This shows that a non-zero extinction coefficient leads to an exponential decay of the wave in

the medium. The intensity is proportional to the square of the amplitude of the field, namely  $I \sim E E^* = E_0^2 e^{-\frac{2K\omega z}{c}}$ . Comparing this with Beer's law shows:

$$\alpha = \frac{2K\omega}{c} = \frac{4\pi K}{\lambda}$$

We can relate the refractive index of a medium to its relative dielectric constant  $\epsilon_r$  by using the standard result derived from Maxwell's equations:  $n = \sqrt{\epsilon_r}$ .

Consequently, when  $n$  is complex,  $\epsilon_r$  must also be complex. We define the complex relative dielectric constant or complex dielectric function  $\tilde{\epsilon}_r = \epsilon_1 + i\epsilon_2$  and

have by analogy:  $\tilde{n}^2 = \tilde{\epsilon}_r$

Using  $\tilde{n} = n + iK$ ,  $\tilde{\epsilon}_r = \epsilon_1 + i\epsilon_2$ , and  $\tilde{n}^2 = \tilde{\epsilon}_r$  we can find:

$$\begin{cases} \epsilon_1 = n^2 - K^2 \\ \epsilon_2 = 2nK \end{cases}$$

$$\text{and } \begin{cases} n = \frac{1}{\sqrt{2}} \sqrt{\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}} \\ K = \frac{1}{\sqrt{2}} \sqrt{-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}} \end{cases}$$

For weak absorption,  $K \ll 1$  we have

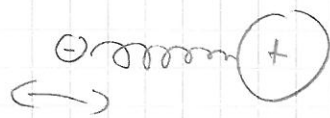
$$n = \sqrt{\epsilon_1} \quad ; \quad K = \frac{\epsilon_2}{2n}$$

so the refractive index is mainly determined by the real part of the dielectric constant, while the absorption is mainly determined by the imaginary part.



The experimental goal is then to determine  $\vec{\epsilon}_r$  or  $\vec{n}$  by measuring  $T$  and  $R$ . Before we take a look at the experiments, however, we will first derive a model for the propagation of light in medium.

We will treat the optically active components in the solid as dipole oscillators (Lorentz oscillator), for example an electron oscillating along its bond to the nucleus:



The frequency of such an oscillation is given by  $\omega_0 = \sqrt{\frac{ks}{\mu}}$ .  $ks$  is the spring constant, and  $\mu$  is the reduced mass,  $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ .

This dipole interacts with electromagnetic radiation: A wave can excite a dipole and consequently lose intensity, and an excited dipole can emit radiation.

The real physical nature of the dipole is not so important right now, we can think of atomic oscillators (electron vs atom), vibrational oscillators (cation vs. anion), or free electron oscillators (vibrations of the free electron gas - Drude-Lorentz model).

Now, we consider the interaction between a light wave and a dipole oscillator

with a single resonant frequency  $\omega_0$ . We model the displacement of the dipole as a damped harmonic oscillation. When we focus to the case of atomic oscillation, it is sufficient to replace the reduced mass by the mass of the electron (i.e. we ignore the motion of the nucleus). We can then write:

$$m_0 \frac{d^2 x}{dt^2} + m_0 \gamma \frac{dx}{dt} + m_0 \omega_0^2 x = -e E,$$

where  $\gamma$  is the damping rate,  $e$  is the elementary charge, and  $E$  is the electric field of the light wave, which we describe by:

$$E(t) = E_0 \cos(\omega t + \phi) = E_0 \operatorname{Re} \left\{ e^{-i(\omega t + \phi)} \right\}$$

The steady state solution is a forced oscillation of the dipole with the frequency of the incident light:

$$x(t) = X_0 \operatorname{Re} \left( e^{-i(\omega t + \phi')} \right)$$

We can get rid of the phase by allowing  $E_0$  and  $X_0$  to be complex. Putting the ansatz into the equation for the damped and forced oscillator yields:

$$X_0 = \frac{-e E_0 / m_0}{\omega_0^2 - \omega^2 - i \gamma \omega}$$

This oscillating dipole gives a resonant contribution to the macroscopic polarization (dipole moment per unit volume). If  $N$  is the number of atoms per volume,

$$\Rightarrow (\epsilon_{st} - \epsilon_{\infty}) = \frac{Ne^2}{\epsilon_0 m_0 \omega_0^2}$$

Finally, we approximate for frequencies close to resonance with  $\omega \approx \omega_0 \Rightarrow \gamma$  and use

$$\Delta\omega = (\omega - \omega_0) :$$

$$\epsilon_1(\Delta\omega) = \epsilon_{\infty} - (\epsilon_{st} - \epsilon_{\infty}) \frac{2\omega_0 \Delta\omega}{4(\Delta\omega)^2 + \gamma^2}$$

$$\epsilon_2(\Delta\omega) = (\epsilon_{st} - \epsilon_{\infty}) \frac{\gamma \omega_0}{4(\Delta\omega)^2 + \gamma^2}$$

These equations describe a sharp atomic absorption line centered at  $\omega_0$  with full width at half maximum equal to  $\gamma$ .

The slide shows the frequency dependence of  $\epsilon_1$  and  $\epsilon_2$  predicted by the above equations for certain values of  $\omega_0$  and  $\gamma$  as well as  $\epsilon_{st}$  and  $\epsilon_{\infty}$ . We see that  $\epsilon_2$  is a strongly peaked function of  $\omega$  with a maximum value at  $\omega_0$ . The frequency dependence of  $\epsilon_1$  is more complicated.

As we approach  $\omega_0$  from below,  $\epsilon_1$  gradually rises from  $\epsilon_{st}$  and reaches a peak at  $\omega_0 - \gamma/2$ . It then falls sharply, passing through a minimum at  $\omega_0 + \gamma/2$  before rising to the high-frequency limit  $\epsilon_{\infty}$ . These line shapes are also called Lorentzian.

Also shown are the more accessible data for  $m$  and  $K$ .

we can write:

dipole moment of single oscillator

$$\begin{aligned} P_{\text{res}} &= N p \\ &= -N e x \\ &= \frac{N e^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i \gamma \omega)} E \end{aligned}$$

Due to the form of the equation,  $P_{\text{res}}$  is small unless the frequency  $\omega$  is close to  $\omega_0$ .

Using  $D = \epsilon_0 E + P$ , we split  $P$  in the resonant and a background term:

$$\begin{aligned} D &= \epsilon_0 E + P_{\text{backgr.}} + P_{\text{res}} \\ &= \epsilon_0 E + \epsilon_0 \chi E + P_{\text{res}} \end{aligned}$$

↑ electric susceptibility

$$\stackrel{!}{=} \epsilon_0 \epsilon_r E$$

$$\Rightarrow \boxed{\epsilon_r(\omega) = 1 + \chi + \frac{N e^2}{\epsilon_0 m_0} \frac{1}{(\omega_0^2 - \omega^2 - i \gamma \omega)}}$$

This can be split into the real and the imaginary part:

$$\epsilon_1(\omega) = 1 + \chi + \frac{N e^2}{\epsilon_0 m_0} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma \omega)^2}$$

$$\epsilon_2(\omega) = \frac{N e^2}{\epsilon_0 m_0} \frac{\gamma \omega}{(\omega_0^2 - \omega^2)^2 + (\gamma \omega)^2}$$

To understand the complex dielectric function better, we first look at the low- and high frequency limit:

$$\epsilon_r(\omega) = \epsilon_{\text{stat}} = 1 + \chi + \frac{N e^2}{\epsilon_0 m_0 \omega_0^2}$$

$$\epsilon_r(\infty) = \epsilon_{\infty} = 1 + \chi$$



In general, an optical medium will have many characteristic resonance frequencies. This can be treated in the model by just adding the contributions to  $\mathbf{P}$  from each mode, see [slide]. Typically, atomic vibrations are in the visible and ultraviolet range, whereas vibronic excitations are in the infrared regime. We can understand this behaviour by starting at high frequencies. Here, the electrons are too slow to respond to the driving field. The medium therefore has no polarization and the dielectric constant is unity. By going down, we pass the characteristic peaks of the Lorentz oscillators with a peak in the absorption spectrum and a wiggle in the refractive index. In between the medium is transparent. The value of the refractive index in the transparent regions gradually increases as we go through more and more resonances on decreasing the frequency, caused by the fact that  $\epsilon_{st} > \epsilon_{\infty}$  which implies that  $n$  is larger below an absorption line than above it. We can compare this to experiment, e.g.  $\text{SiO}_2$  (glass), see [slide], which compares well to the simple model regarding the general features. To finish this theoretical introduction, it is important to

state that  $n(\omega)$  and  $k(\omega)$  are not independent quantities, but can be calculated from each other using the Kramers-Kronig relationships. This can be very useful in practice, because one could get the dispersion from an absorption experiment and vice versa.

Now we will turn to experiment by first discussing the measurement of absorption spectra.

The easiest way to measure the absorption coefficient of a material is to make a transmission experiment on a thin platelet sample.

However, as the absorption coefficient varies by several orders of magnitude according to the wavelength, this can be more difficult than it sounds. A platelet which absorbs almost nothing for a certain wavelength (too thin) may absorb almost everything for another (too thick). Usually, it is necessary to combine several techniques to determine the absorption accurately over a wide range of photon energies.

The slide illustrates the basic principles of transmission and reflection measurements. Light from a white-light source is filtered by a monochromator and is incident on the sample. (See slide for the example of a Czerny-Turner monochromator). The transmitted and reflected light is recorded by

detectors as the photon energy is changed by scanning the monochromator. The choice of source and detector for a particular experiment depends on the spectral region in which the measurements are being made [slide]. A black body emitter such as a tungsten bulb can be used as the source for measurements in the visible or infrared spectral regions, but at higher frequencies X-ray lamps or other specialized UV-sources must be used. Photomultiplier tubes can be used as the detector for the visible and ultraviolet regions [slide]. For long wave lengths, semiconductor photodiodes are used. For measurements in the infrared or far in the ultraviolet, the apparatus must be enclosed within a vacuum chamber to prevent absorption by the air molecules.

The measurement mode introduced above is also called the dispersive mode. Modern spectrometers, especially for the infrared regime, use polychromatic light and deconvolute the measured signal after the sample using Fourier transformation (Fourier-transform infrared spectroscopy), thereby measuring all frequencies simultaneously. (slide). The main advantages are better signal-to-noise ratio, more light intensity, and less complicated mechanics.