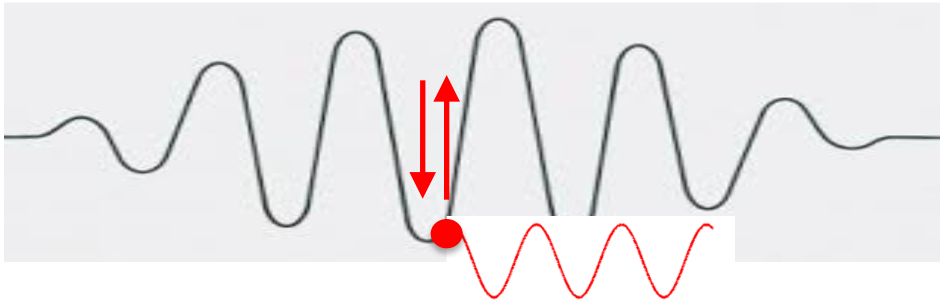


macroscopically…

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$

$$\vec{P} = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} EE + \varepsilon_0 \chi^{(3)} EEE + \ \ldots$$

$\varepsilon_0 \chi^{(1)} E$	$\varepsilon_0 \chi^{(2)} EE$	$\varepsilon_0 \chi^{(3)} EEE$
Absorbance	SFG (SHG)	SFG (THG)
Refraction	DFG	DFG
Reflection	…	Pump-probe techniques
		…

microscopically…

$$\vec{\mu} = \alpha E + \beta EE + \gamma EEE + \ \ldots$$

α: Polarizability = molecular volume

β: Iper-polarizability = molecular asimmetry

The linear term:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 (1+\chi)\vec{E} = \varepsilon \vec{E}$$

$$\varepsilon = \varepsilon_r \varepsilon_0 = (1+\chi)\varepsilon_0$$

ε electric permittivity

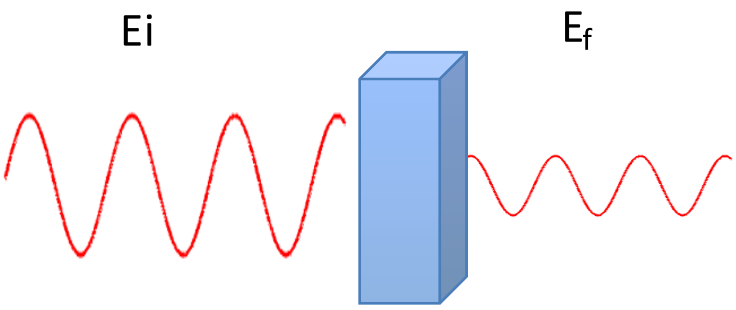
χ electric susceptibility of the dielectric

ε and χ are scalars in homogeneous isotropic media and 2nd rang tensors in anisotropic media:

$$\vec{P} = \varepsilon_0 \begin{pmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{pmatrix} \begin{pmatrix} \vec{E}_x \\ \vec{E}_y \\ \vec{E}_z \end{pmatrix}$$

Susceptivity takes on both real and imaginary part.

Absorbance depends on the imaginary part of susceptivity:



$$\nabla E = \varepsilon\mu_0 \frac{\partial^2 E}{\partial t^2}$$ plane wave eq.

$$E_f = E_0 e^{i(kz-\omega t)}$$

- Angular frequency ω doesn't change,
- Wave vector k changes in a dielectric:

$$f\lambda = v$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi f}{v} = \omega\sqrt{\varepsilon\mu_0} = \omega\sqrt{\varepsilon_0\mu_0(1+\chi)} = \frac{\omega}{c}\sqrt{1+\chi}$$

$$\left(\frac{kc}{\omega}\right)^2 = 1+\chi$$

Wave dispersion eq.in a dielectric

$$(\eta + ib)^2 = 1 + \chi' + i\chi''$$

NB: $\eta = \frac{c}{v} = \frac{\sqrt{\varepsilon \quad \mu_0}}{\sqrt{\varepsilon_0 \mu_0}} = \sqrt{1 + \chi}$

$\eta^2 - b^2 = 1 + \chi'$ Real part

$2\eta b = \chi''$ Imaginary part

$$k = \frac{\omega}{c}(\eta + ib)$$

$$E_f = E_0 e^{i(kz - \omega t)} = E_0 \ e^{i(\frac{\omega}{c}\eta\, z + i\frac{\omega}{c} b\, z - \omega t)} = E_0 \ e^{i(\frac{\omega}{c}\eta\, z - \omega t)} e^{-\frac{\omega}{c} b\, z}$$

Outcoming oscillating field

Real exponential decay due to sample absorption.

$$I \propto E^2$$

$$I_T = I_0 e^{-2\frac{\omega}{c} b\, z}$$

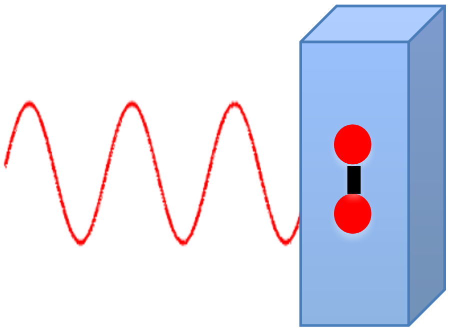
$$A = -log\frac{I_T}{I_0} = (\log e)\, 2\frac{\omega}{c} b\, z = \varepsilon_{extinct} \cdot z$$

Extinction coefficient for one oscillator at one frequency

b = coefficient of the imaginary part of refractive index

$$\varepsilon_{extinct} = 2(\log e)\frac{\omega}{c}\ b$$

The natural bandwidth of the absorbance band as a lorentzian shape!



Damped and forced harmonic oscillator:

$$m\ddot{x} + \Gamma\dot{x} + kx = -eE_0 e^{-i\omega t}$$

$\vec{R} = -\Gamma\vec{v}$ Retarding force
Γ = natural damping coefficient

$\overrightarrow{F_r} = -k\vec{x}$ Restoring force of the harmonic oscillator

$$\omega_0 = \sqrt{\frac{k}{m}}$$

$\overrightarrow{F_{el}} = -e\vec{E}$ Electric driving force of the applied field

$$x(t) = Ae^{-i\omega t}$$

Molecule oscillates at the field frequency

$$A = \frac{-eE_0}{m(\omega_0^2 - \omega^2 - i\omega\Gamma)}$$

Considering different central natural frequencies of several molecules in solution…

$$A = \frac{-eE_0}{m} \cdot \sum_i \frac{f_i}{\left(\omega_{0i}^2 - \omega^2 - i\omega\Gamma_i\right)}$$

f_i = fraction of oscillators at frequency i

Total polarization in a macroscopic homogeneous sample is:

$$\mathrm{P}(\omega) = \frac{-eN}{V} \cdot A = \frac{e^2 N E_0}{mV} \cdot \frac{1}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}$$

$$\mathrm{P} = \varepsilon_0 \chi E$$

$$\chi(\omega) = \frac{e^2 N}{mV\varepsilon_0} \cdot \frac{1}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}$$

Divide real and imaginary part:

$$\chi(\omega) = \frac{e^2 N}{mV\varepsilon_0}\left[\frac{1}{(\omega_0^2 - \omega^2 - i\omega\Gamma)} \cdot \frac{(\omega_0^2 - \omega^2 + i\omega\Gamma)}{(\omega_0^2 - \omega^2 + i\omega\Gamma)}\right]$$

$$\chi(\omega) = \frac{e^2 N}{mV\varepsilon_0}\left[\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 - (i\omega\Gamma)^2} + \frac{i\omega\Gamma}{(\omega_0^2 - \omega^2)^2 - (i\omega\Gamma)^2}\right]$$

$$\chi(\omega) = \frac{e^2 N}{mV\varepsilon_0}\left[\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 - (i\omega\Gamma)^2} + \frac{i\omega\Gamma}{(\omega_0^2 - \omega^2)^2 - (i\omega\Gamma)^2}\right]$$

$$(\eta + ib)^2 = 1 + \chi' + i\chi''$$

$$2\eta b = \chi''$$

$$2\eta b = \frac{e^2 N}{mV\varepsilon_0}\left[\frac{\omega\Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2}\right]$$

$$\varepsilon_{extinct} = 2(\log e)\frac{\omega}{c} b$$

$$\varepsilon_{extinct} = 2(\log e)\frac{\omega}{c}\, b = 2(\log e)\frac{\omega}{c}\cdot\frac{1}{2\eta}\cdot\frac{e^2 N}{mV\varepsilon_0}\left[\frac{\omega\Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2}\right]$$

$$\varepsilon_{extinct} = (\log e)\frac{e^2 N}{mV\varepsilon_0 c\eta}\left[\frac{\omega \quad \Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2}\right]$$

$$S = (\log e)\frac{e^2 N}{mV\varepsilon_0\omega_0}$$

Strength of oscillator ω_0

$$\varepsilon_{extinct} = \frac{S\Gamma}{c\eta}\left[\frac{\omega \quad \omega_0}{(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2}\right]$$

$$\varepsilon_{extinct} = \frac{S\Gamma}{c\eta}\left[\frac{\omega \quad \omega_0}{(\omega_0 - \omega)^2(\omega_0 + \omega)^2 + \omega^2\Gamma^2}\right]$$

When damping Γ is small and $\omega \approx \omega_0$:

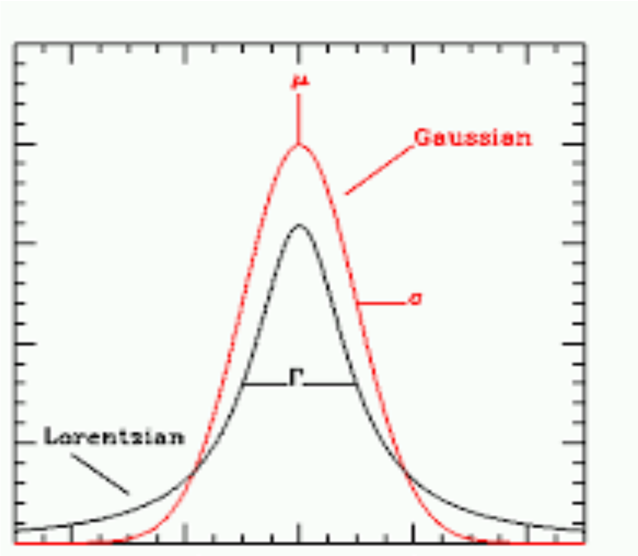
$$\varepsilon_{extinct} = \frac{S\Gamma}{c\eta}\left[\frac{{\omega_0}^2}{(\omega_0 - \omega)^2 \cdot 4\omega^2 + \omega^2\Gamma^2}\right]$$

$$\varepsilon_{extinct} = \frac{S\Gamma\omega_0^2}{4c\eta}\left[\frac{1}{(\omega_0 - \omega)^2 + \left(\frac{\Gamma}{2}\right)^2}\right]$$

Amplitude ε_0 proportional to oscillator strenght

Γ is the bandwidth

LORENTZIAN EQUATION



'Till now:

The linear term…

- Absorbance depends on the imaginary part of the refractive index (linear susceptivity);
- Natural width of the absorbance band as a lorentzian profile.

Non-linear terms of induced polarization!!!

$$\vec{P} = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} EE + \varepsilon_0 \chi^{(3)} EEE + \ \dots$$

SFG (SHG)
DFG
Light rettification

SFG (THG)
DFG
Mixing frequency
Fluorescence
Two-photon absorption
Raman and Rayleigh scattering

In all effects, the outcoming field oscillates at a different frequency from the incoming field

The second term:

$$\overrightarrow{P^{(2)}} = \chi^{(2)}\vec{E}\vec{E}$$

$$\vec{E} = \vec{E}_0 \cos \omega t$$

Two incoming equal fields
(high photon density with lasers)

→ Second harmonic generation (SHG in BBO)

→ Light rectification (time domain)

$$\overrightarrow{P^{(2)}} = \chi^{(2)}\vec{E}_0^2 \cos^2 \omega t = \chi^{(2)}\vec{E}_0^2 \cdot \frac{\cos(2\omega t) + \cos 0}{2}$$

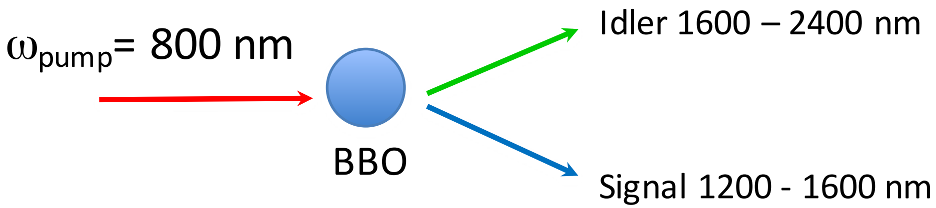
Different fields
(O.P.A.)

→ Sum frequency generation

→ Difference frequency generation

$$\overrightarrow{P^{(2)}} = \chi^{(2)}\vec{E}_1\vec{E}_2 \cos \omega_1 t \cos \omega_2 t = \chi^{(2)}\vec{E}_1\vec{E}_2 \frac{\cos(\omega_1+\omega_2)t + \cos(\omega_1-\omega_2)t}{2}$$

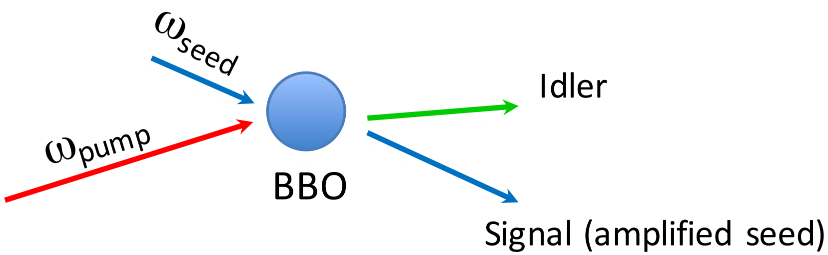
Optical parametric generation (OPG):



$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

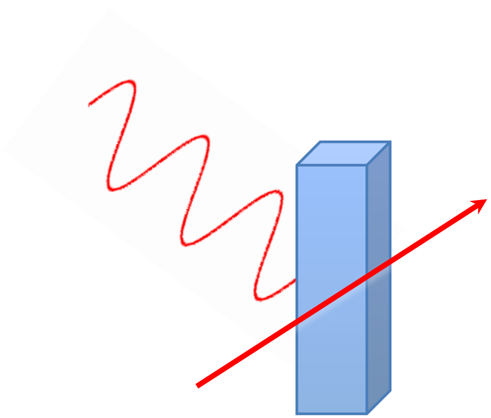
Special non-linear 2nd order optical effects:

Optical parametric amplification (OPA)



Generation of IR pulses from fs Ti:Sa 800 nm laser output.

Pockel cells



Continuous $\vec{E}$ modifies η

Second field feels a different index of refraction of the material. Ex: turn of polarization.

NO 2nd order effects in isotropic media!!!

(gas, symmetric crystals, homogeneous solutions)

The third term:

$$\overrightarrow{P^{(3)}} = \chi^{(3)}\vec{E}\vec{E}\vec{E}$$

$$\vec{E} = \vec{E}_0 \cos \omega t$$

Three incoming equal fields → Third harmonic generation (266nm)

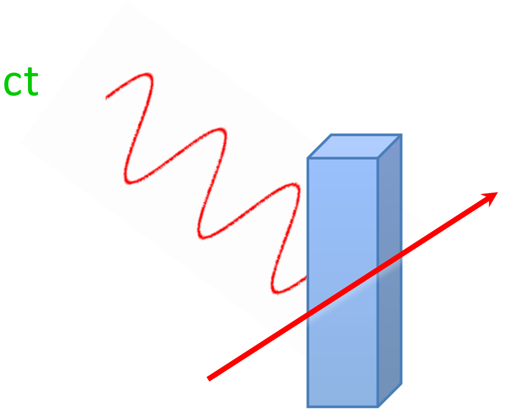
Three incoming equal fields → Rayleigh scattering

$$\overrightarrow{P^{(3)}} = \chi^{(3)}\vec{E}_0^3 \cos^3 \omega t = \chi^{(3)}\vec{E}_0^3 \cdot \frac{\cos(3\omega t) + 3\cos(\omega t)}{4}$$

Different incoming fields → Mixing frequency generation

Special non-linear 3rd order optical effects:

Kerr effect



All materials show a Kerr effect.
In non-symmetric material Pockel effect is stronger!

$$K \propto \overrightarrow{E^2}$$

Modulation of refraction index:

- Self-focusing
- Self-phase modulation
- Kerr-lens mode locking

All pump-prbe techniques: