Optical methods in chemistry
or
Photon tools for chemical sciences

Session 10:

Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- Spectroscopy
- Electromagnetic optics
- **Absorption, dispersion, and non-linear optics**
- Ultrafast lasers
- Introduction to x-rays
- X-ray diffraction and spectroscopy
- Summary

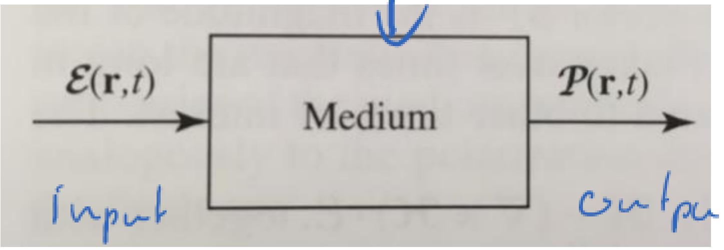
Today:

More materials properties, linear and non-linear

Electromagnetic waves in dielectric media

General

interpretation → output response



in response to an electric field $\mathcal{E}$ media creates a polarization

"instantaneous" "no $\vec{r}$" "no direction"

But stick with linear, nondispersive, homogenous, and isotropic media right now: $\mathcal{E} \rightarrow [M] \rightarrow P$

simplify to

$$\mathcal{P} = \epsilon_o \chi \mathcal{E},$$

→ electric susceptibility

χ scalar

$\mathcal{E} \rightarrow [\chi] \rightarrow P$

$D = \varepsilon \mathcal{E}$ / $\varepsilon = \varepsilon_0 (1+\chi)$

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

↑ dielectric constant

" electric permittivity

This leads to the following Maxwell and wave equations wave equations

$$\nabla \times \mathcal{H} = \epsilon \frac{\partial \mathcal{E}}{\partial t}$$

$$\nabla \times \mathcal{E} = -\mu \frac{\partial \mathcal{H}}{\partial t}$$

$$\nabla \cdot \mathcal{E} = 0$$

$$\nabla \cdot \mathcal{H} = 0.$$

ε – dielectric constant (electric permittivity)

μ – magnetic permeability

back to wave equation

$$\nabla^2 u - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0 \quad \Big| \text{ in medium}$$

$$c = \frac{1}{\sqrt{\varepsilon \mu}}$$

define $n = c_0/c = \sqrt{\frac{\varepsilon}{\varepsilon_0}\frac{\mu}{\mu_0}}$ = refractive index!

non-magnetic materials

$$n = \sqrt{\varepsilon/\varepsilon_0} = \sqrt{1 + \chi}$$

Generalized optical constant

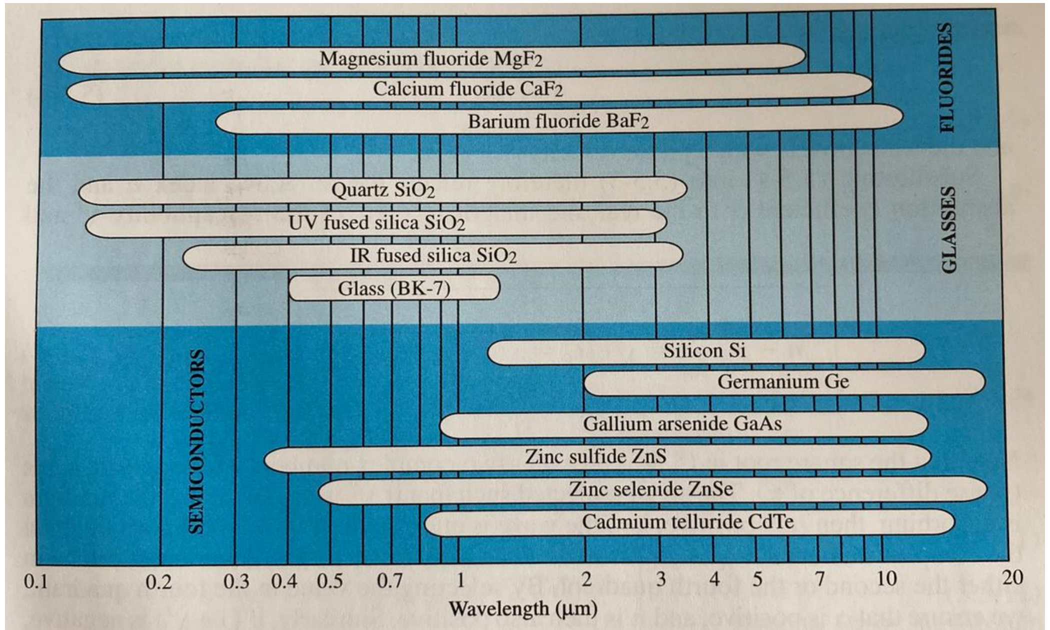


Figure 5.5-1 Spectral bands within which selected optical materials transmit light.

Absorption: The imaginary part

Complex refractive index

General:

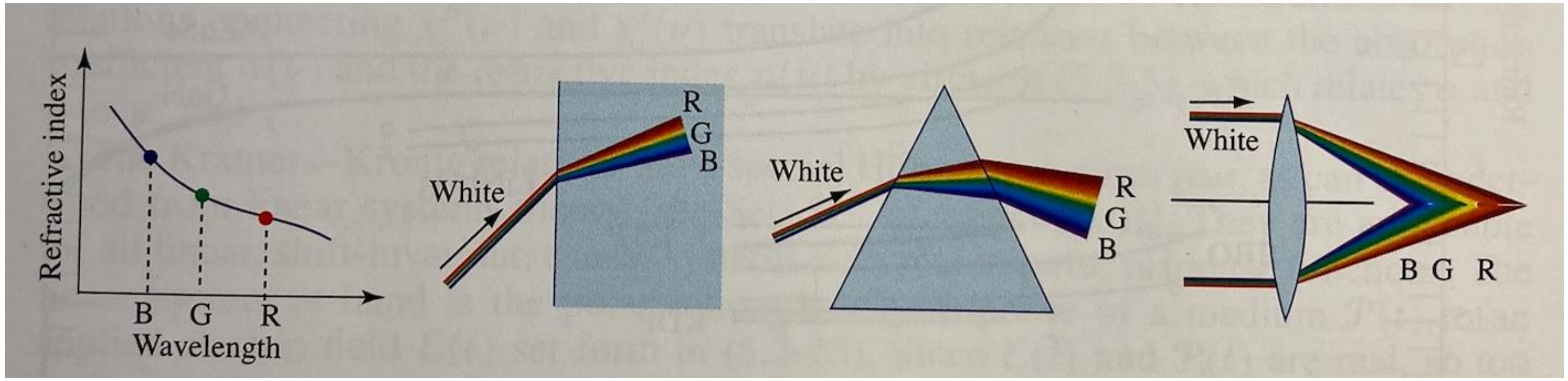
$$n - j\frac{1}{2}\frac{\alpha}{k_o} = \sqrt{\epsilon/\epsilon_o} = \sqrt{1 + \chi' + j\chi''}.$$

Weakly absorbing media:

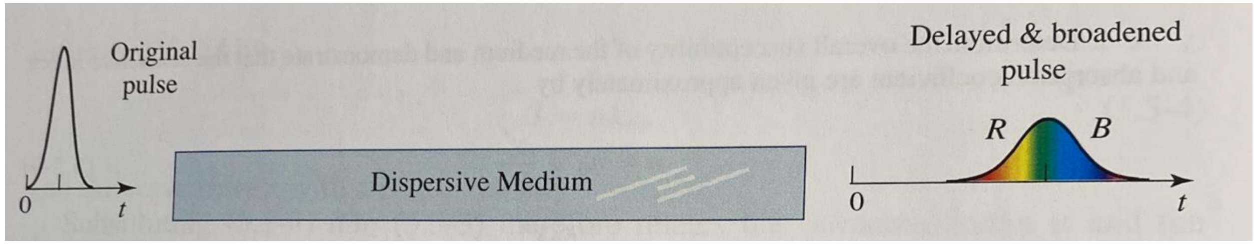
$$n \approx \sqrt{1 + \chi'}$$

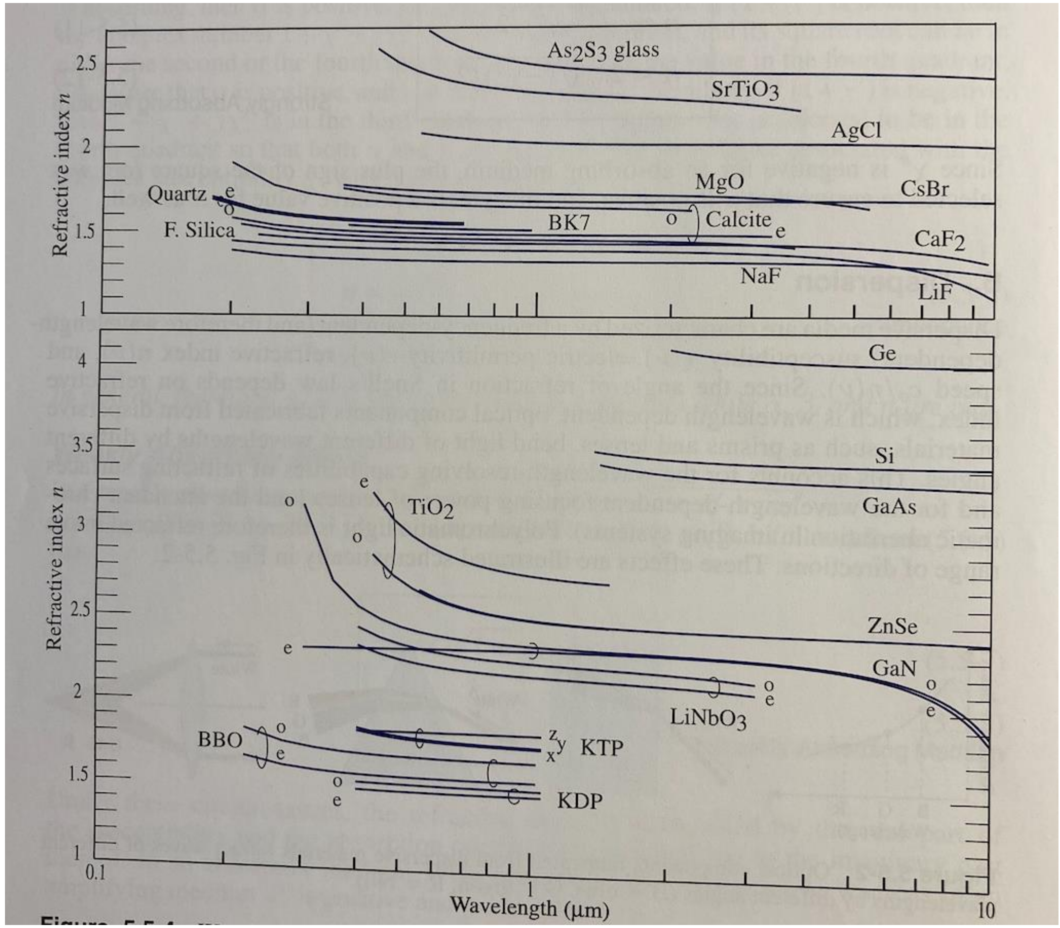
$$\alpha \approx -\frac{k_o}{n}\chi''.$$

Dispersion: The real part



A short pulse in a dispersive medium



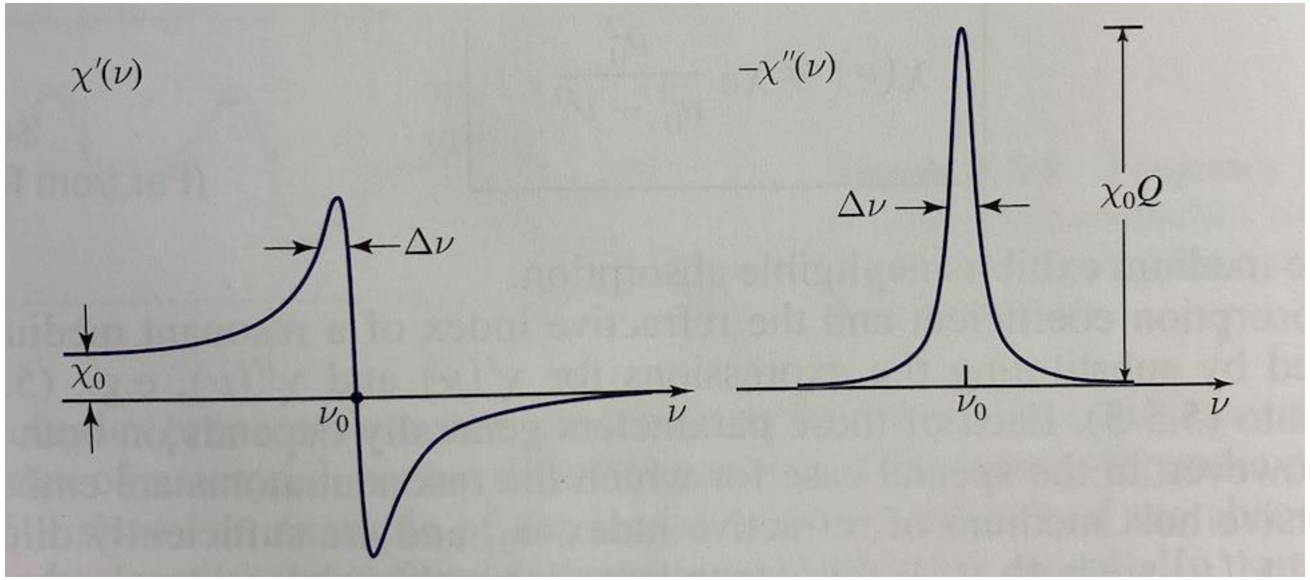


The Kramers-Kronig Relation

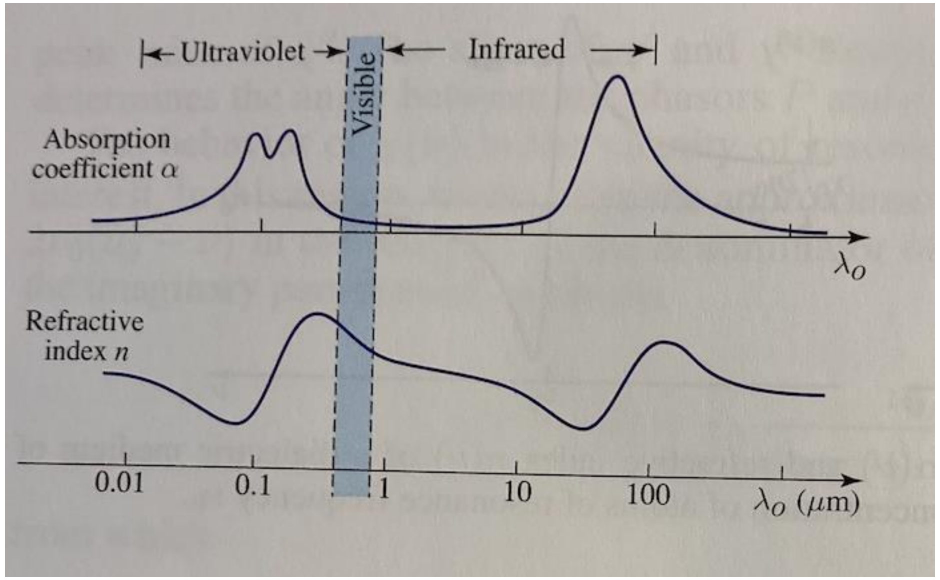
$$\chi'(\nu) = \frac{2}{\pi} \int_0^\infty \frac{s\chi''(s)}{s^2 - \nu^2}\, ds$$

$$\chi''(\nu) = \frac{2}{\pi} \int_0^\infty \frac{\nu\chi'(s)}{\nu^2 - s^2}\, ds.$$

Resonances and refractive index

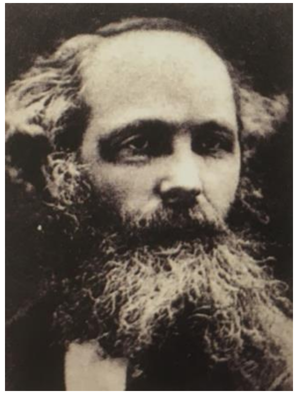


A real optical (transparent) material



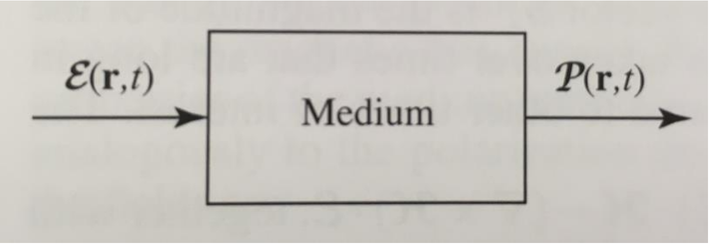
From linear to non-linear

Back to formal description of light as EM wave (from Session 9)



James Maxwell
1831 - 1879

$$\nabla \times \mathcal{H} = \epsilon_o \frac{\partial \mathcal{E}}{\partial t}$$
$$\nabla \times \mathcal{E} = -\mu_o \frac{\partial \mathcal{H}}{\partial t}$$
$$\nabla \cdot \mathcal{E} = 0$$
$$\nabla \cdot \mathcal{H} = 0,$$



But stick with linear, nondispersive, homogenous, and isotropic media right now:

$$\mathcal{P} = \epsilon_o \chi \mathcal{E},$$

$$\nabla \times \mathcal{H} = \epsilon \frac{\partial \mathcal{E}}{\partial t}$$
$$\nabla \times \mathcal{E} = -\mu \frac{\partial \mathcal{H}}{\partial t}$$
$$\nabla \cdot \mathcal{E} = 0$$
$$\nabla \cdot \mathcal{H} = 0.$$

Generalization of susceptibility χ (still linear)

- Inhomogenous media
- Anisotrope media
- Dispersive media

General:

Interpretation: Dynamic relationship between E an P

- E induces bound electrons in material to oscillate
- Time-dependent Polarization density P(t)
- Time-delay between E(t) and P(t)

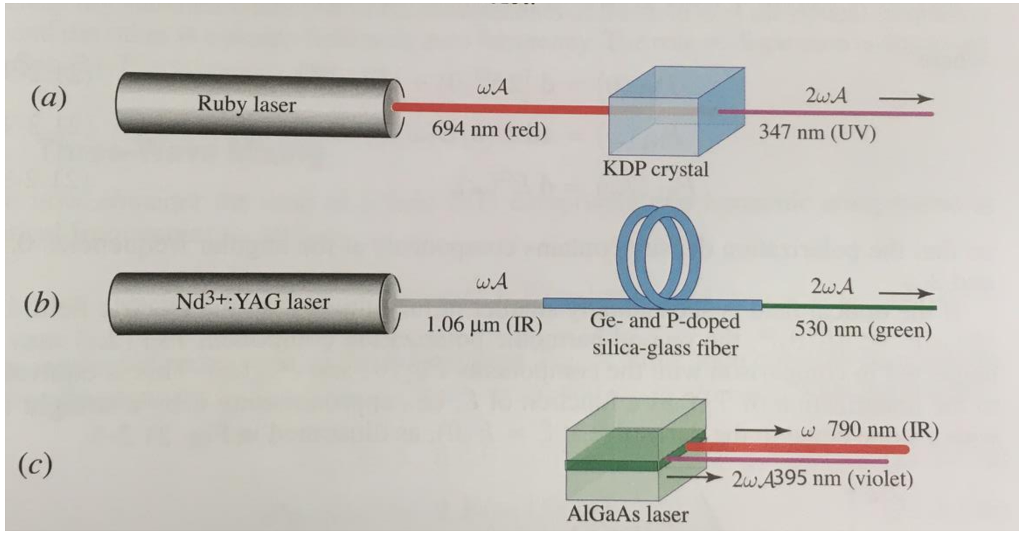
Non-linear optical media

Handwaving:

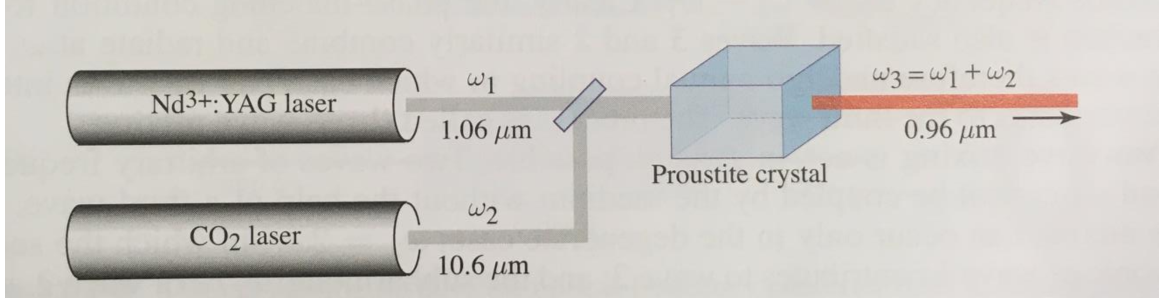
- Linear: restoring force of light induced fields linear ("Hookes law applies")
- Non-linear: Light induced fields comparable to inter-atomic fields in crystal ("no more linear forces")
- (Note: fields still weak compared to intra-atomic fields – that is a later topic)

Expanded description of relationship between Polarization density P and Electric field E

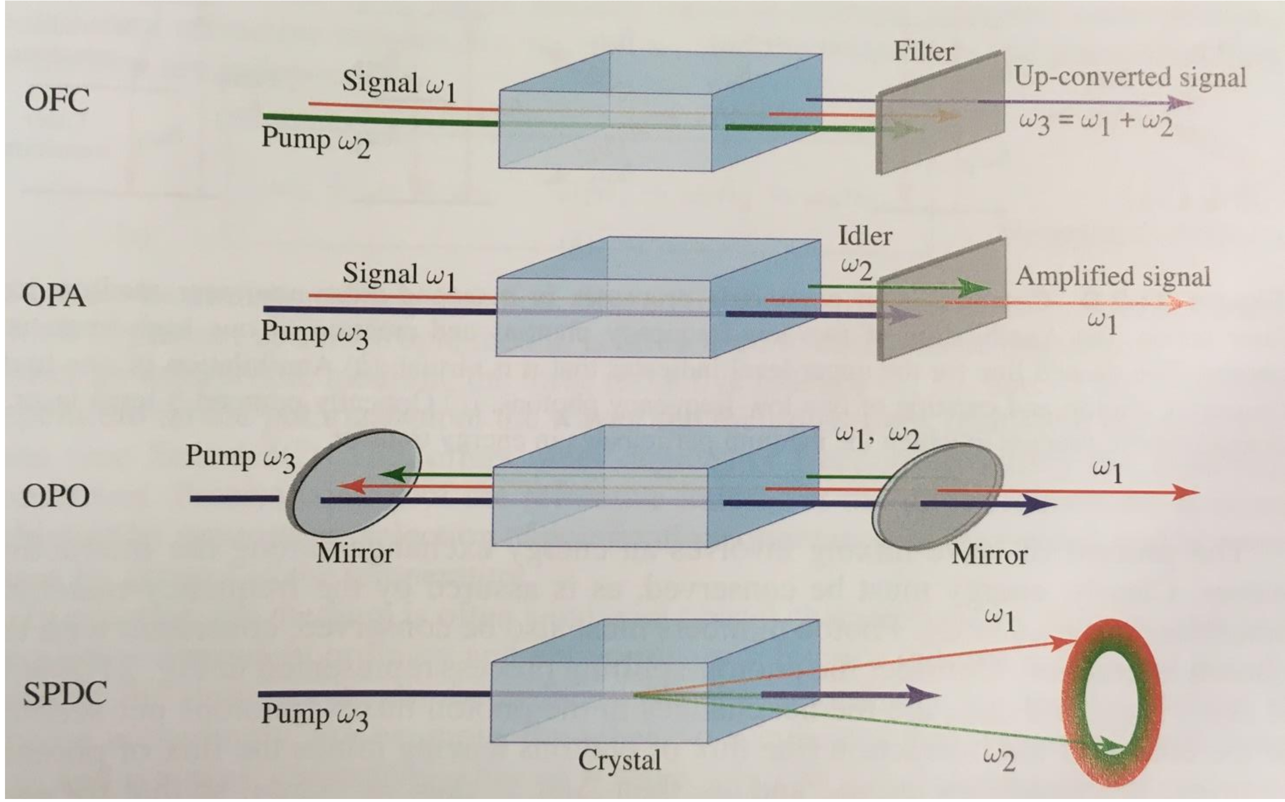
Second order non-linear optics example: Second harmonic generation



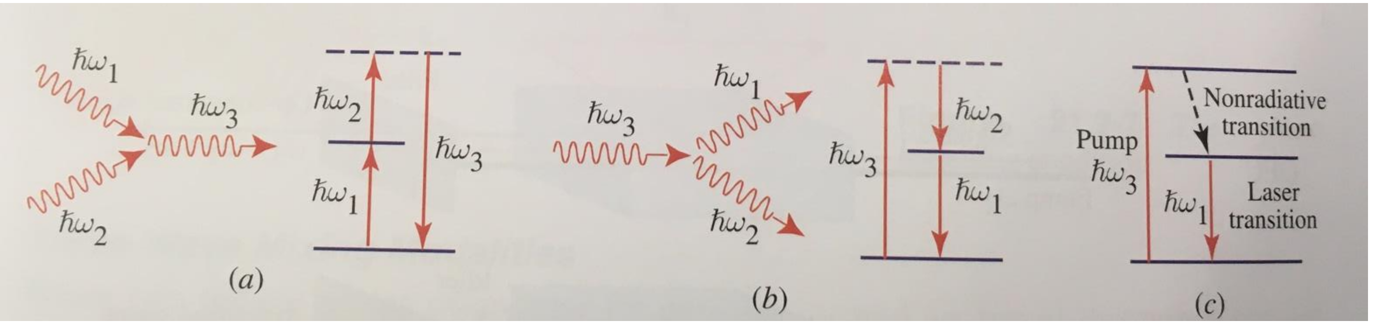
Second order non-linear optics example: Sum frequency generation



Second order non-linear optics example: Optical parametric devices

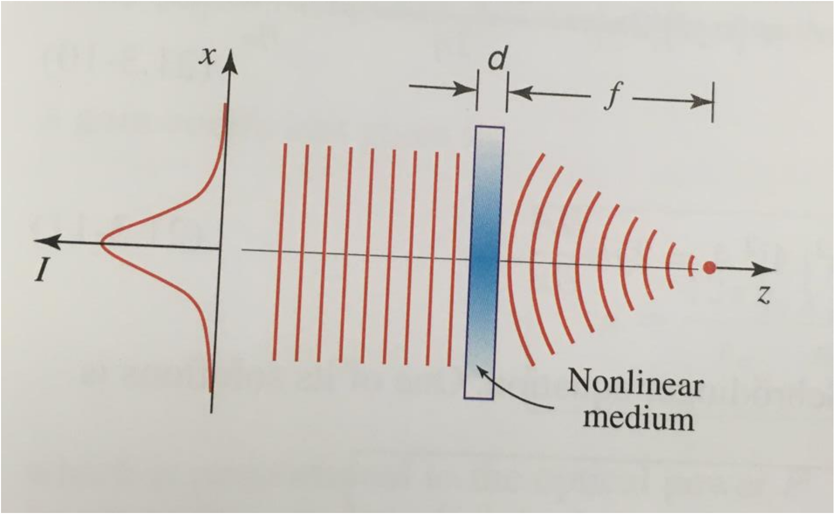


Second order non-linear optics example: Description as photon interaction process

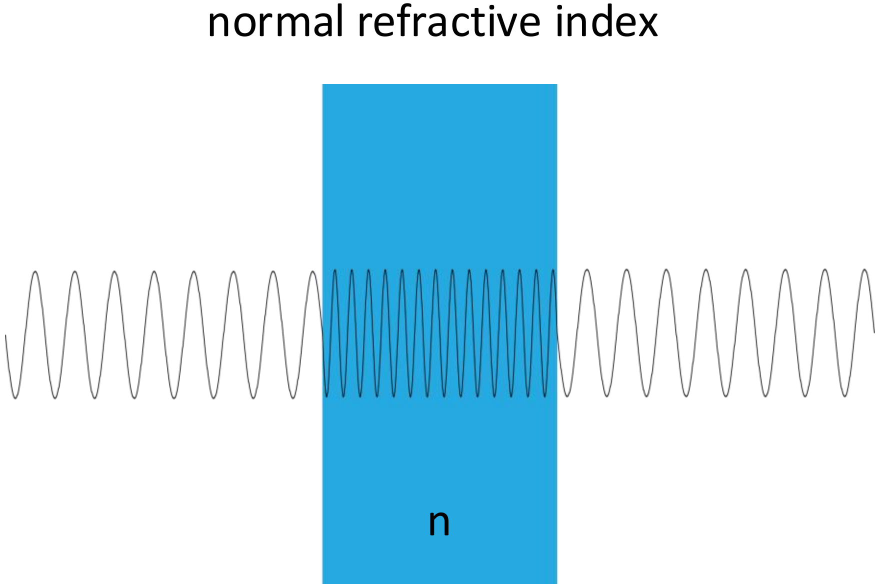


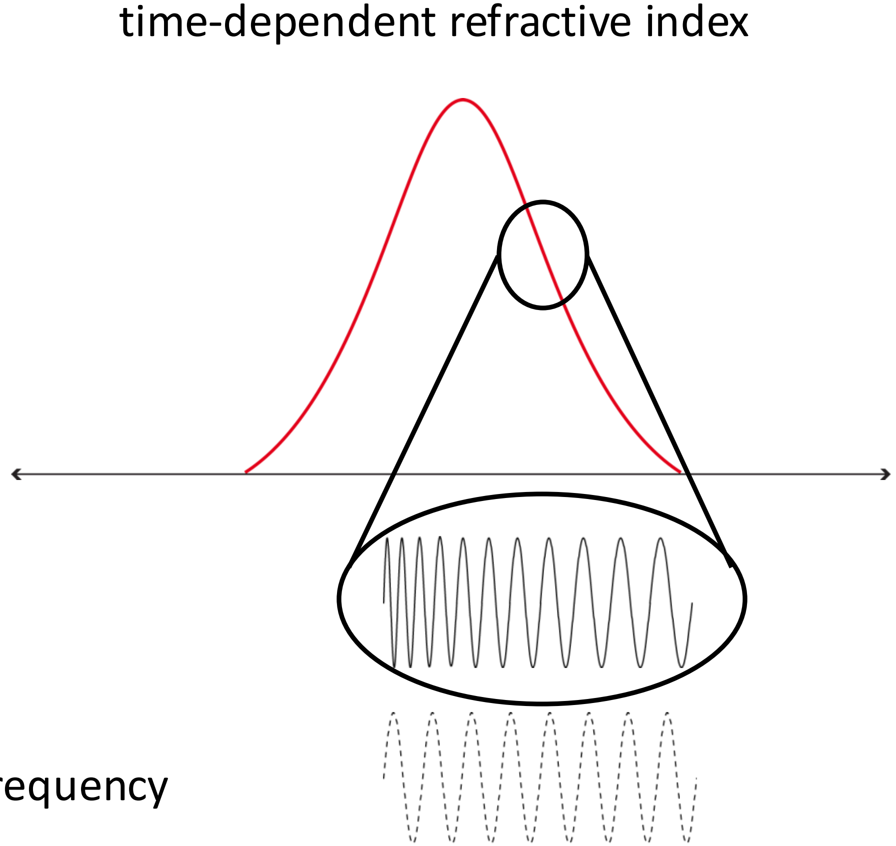
Third order non-linear optics example: Third-harmonic generation

Third order non-linear optics example: Optical Kerr Effect and Self-Focusing



Third order non-linear optics example: Self-phase modulation





$$\omega(t) = -\frac{d\varphi(t)}{dt}$$; instantaneous frequency

- Conceptually – consider a plane monochromatic wave
- Time-dependent index leads to time-dependent frequency
- New frequency components are generated

The end.