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

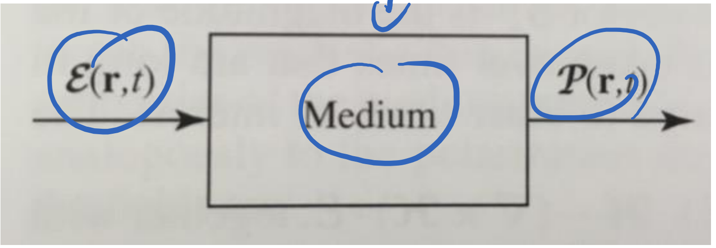
Today:

More materials properties, linear and non-linear

Electromagnetic waves in dielectric media

interpretation: output response

General



in response to an electrical field $\mathcal{E}$
medium creates a polarization

instantaneous — no r — no direction

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

$$\mathcal{E} \to \boxed{M} \to P$$

Simplifies

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

→ electric susceptibility

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

dielectric constant

χ scalar

$$\mathcal{E} \to \boxed{\chi} \to P$$

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

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

μ — magnetic permeability

back to wave equation

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

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

define $n = \dfrac{c_0}{c} = \sqrt{\dfrac{\varepsilon}{\varepsilon_0} \cdot \dfrac{\mu}{\mu_0}}$ = refractive index

non-magnetic materials

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

Homework

familiarize yourself with this kind of e-dynamics

Generalized optical constant

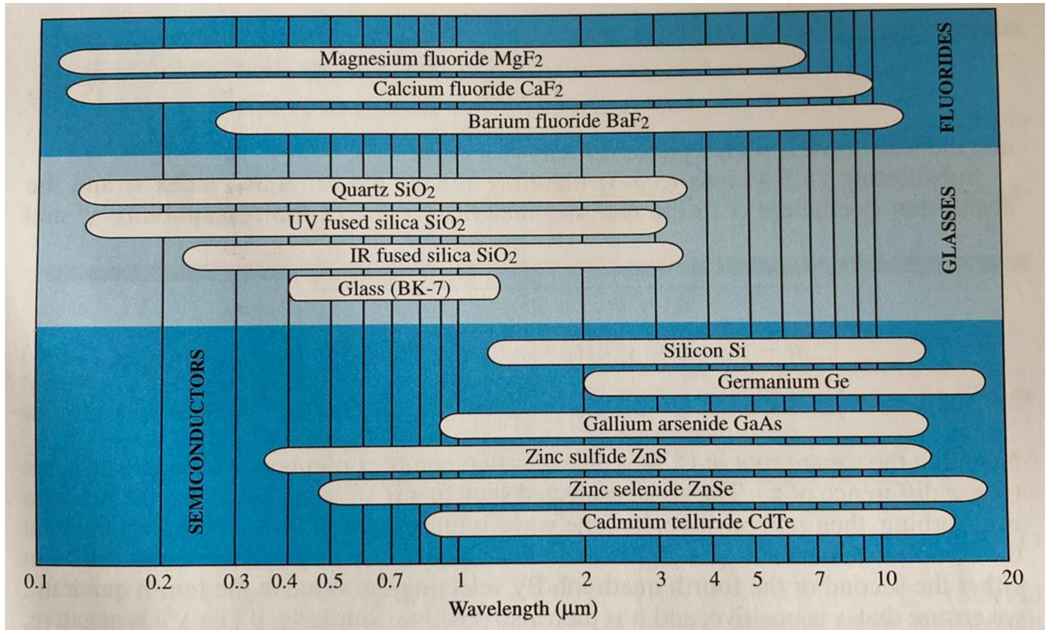


Figure 5.5-1 Spectral bands within which selected optical materials transmit light.

Absorption: The imaginary part

Complex refractive index

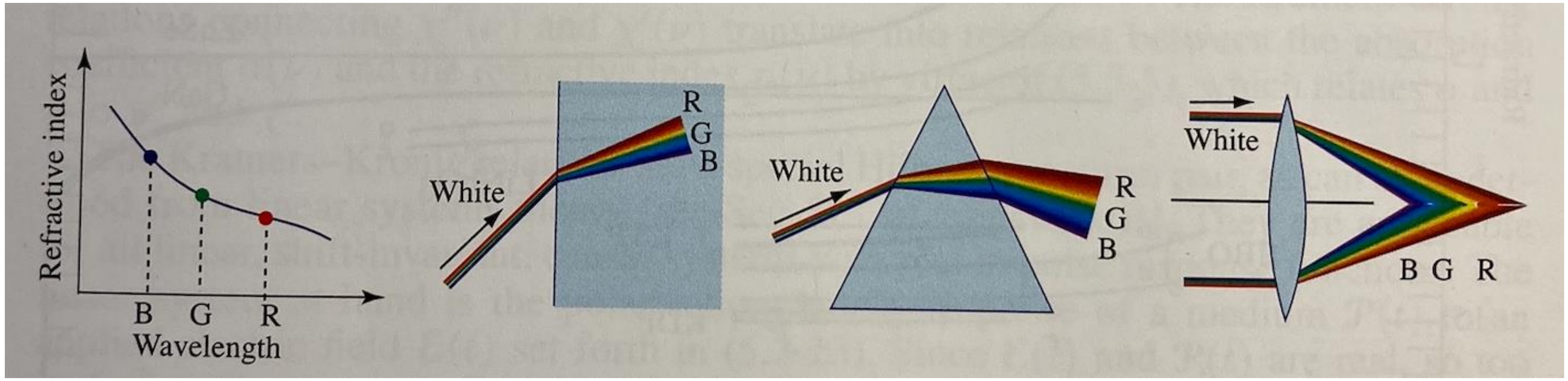
General:

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

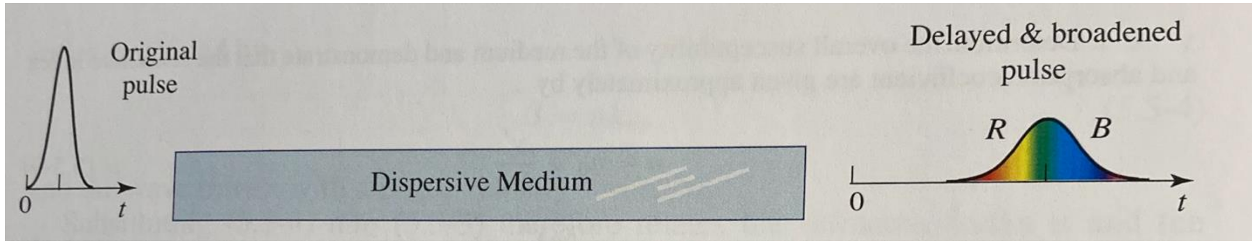
Weakly absorbing media:

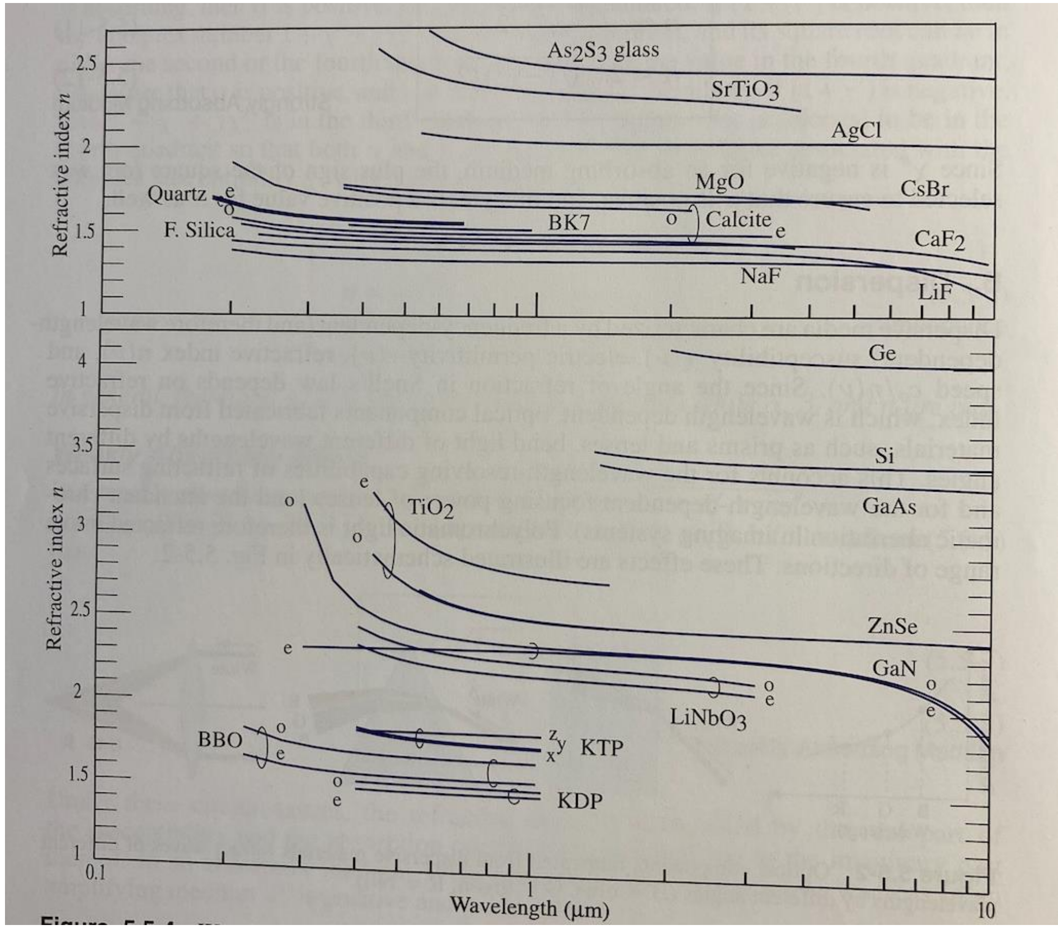
$$\boxed{\begin{aligned} n &\approx \sqrt{1 + \chi'} \\ \alpha &\approx -\frac{k_o}{n}\chi''. \end{aligned}}$$

Dispersion: The real part



A short pulse in a dispersive medium



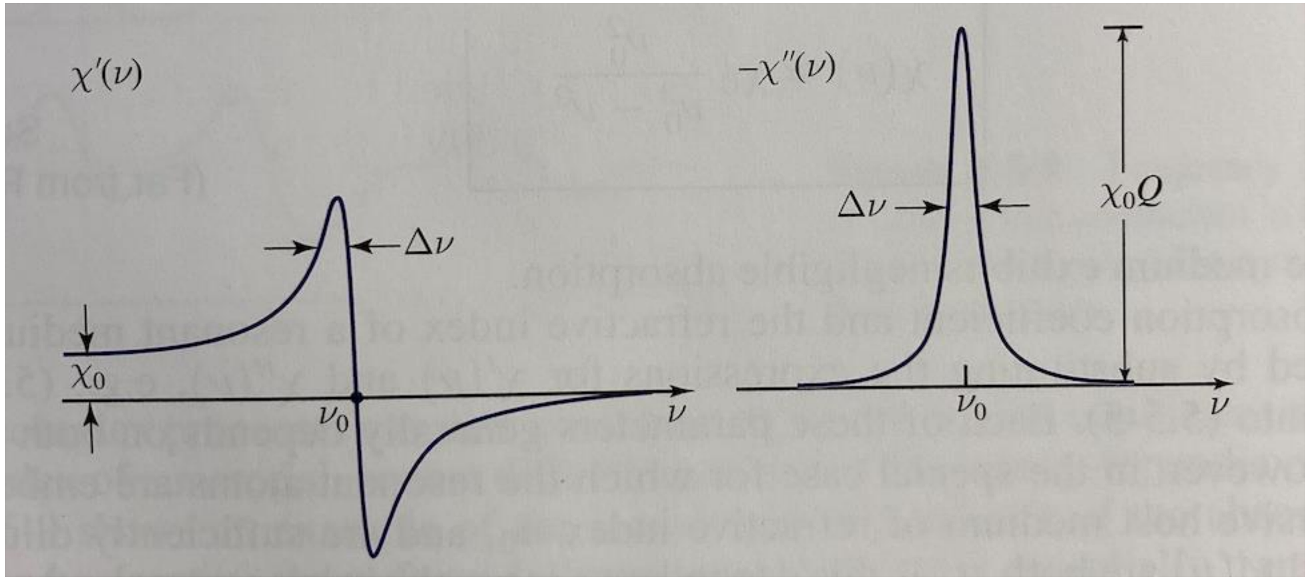


The Kramers-Kronig Relation

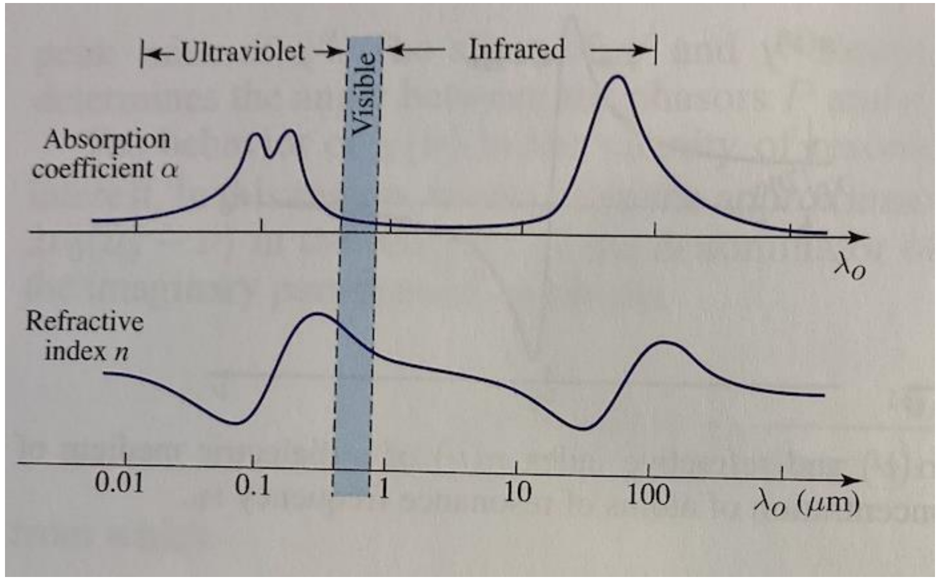
$$\chi'(\nu) = \frac{2}{\pi}\int_0^\infty \frac{s\chi''(s)}{s^2-\nu^2}\,ds$$

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

Resonances and refractive index

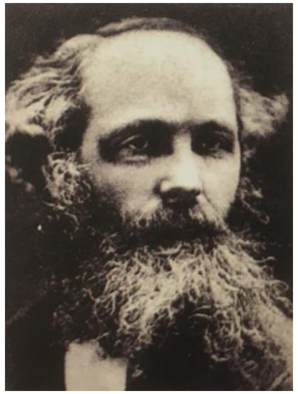


A real optical (transparent) material



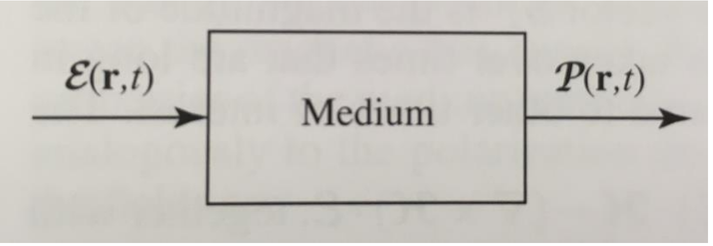
From linear to non-linear

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



James Maxwell
1831 - 1879

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



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

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

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

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)

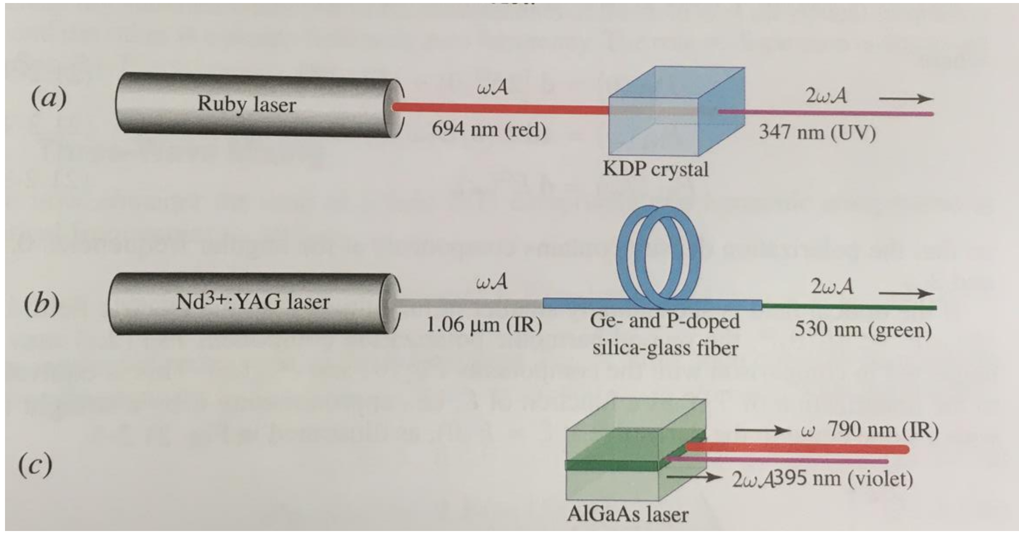
Non-linear optical media

Handwaving:

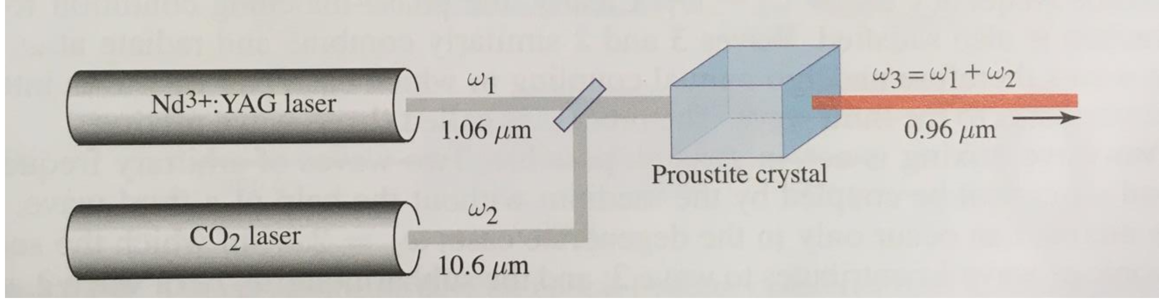
- Linear: restoring force of light induced fields linear (“Hookes law applies”)
- Non-linear: Light induced fields comparable to inter-atomic fields in crystal (”no more linear forces”)
- (Note: fields still weak compared to intra-atomic fields – that is a later topic)

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

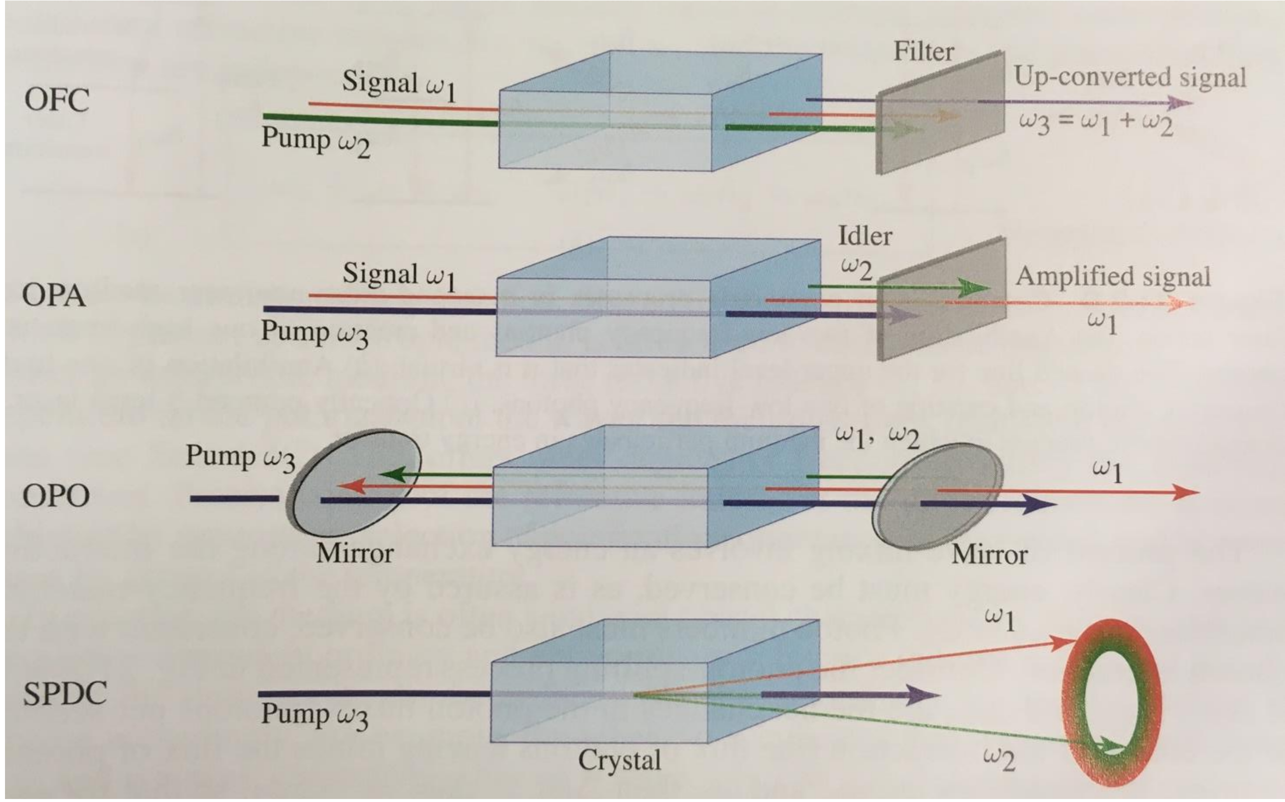
Second order non-linear optics example: Second harmonic generation



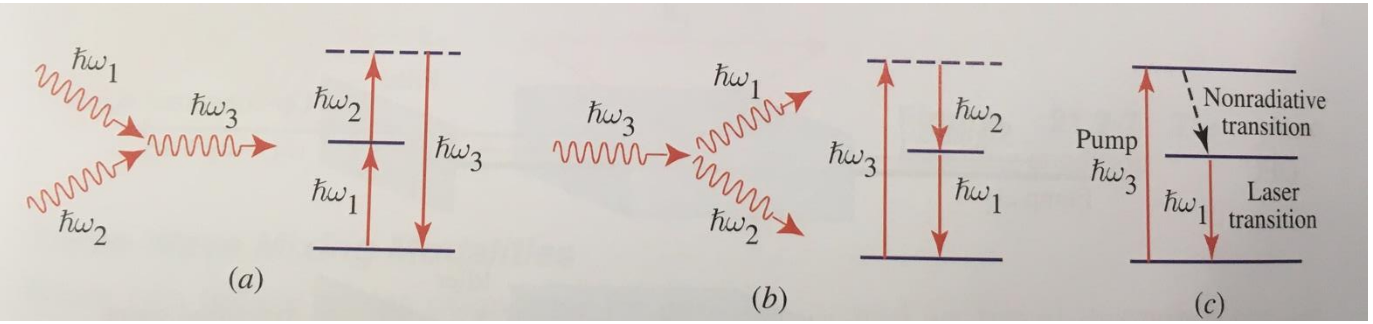
Second order non-linear optics example: Sum frequency generation



Second order non-linear optics example: Optical parametric devices

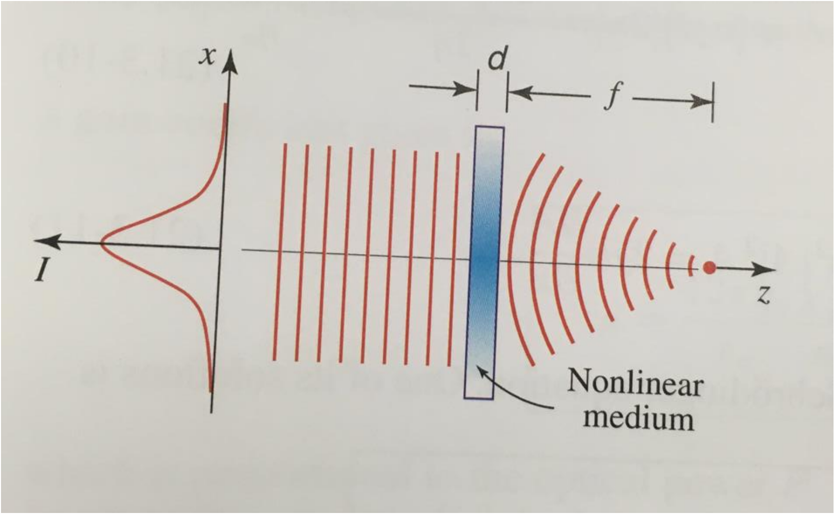


Second order non-linear optics example: Description as photon interaction process



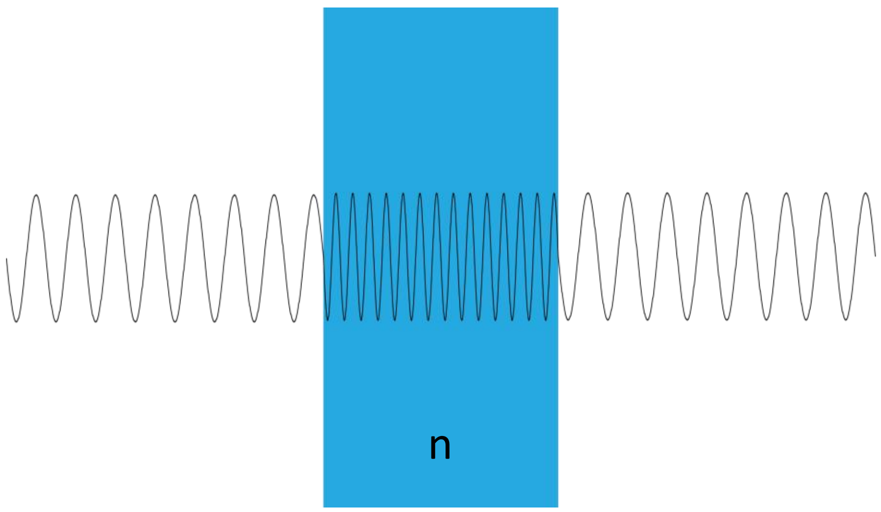
Third order non-linear optics example: Third-harmonic generation

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

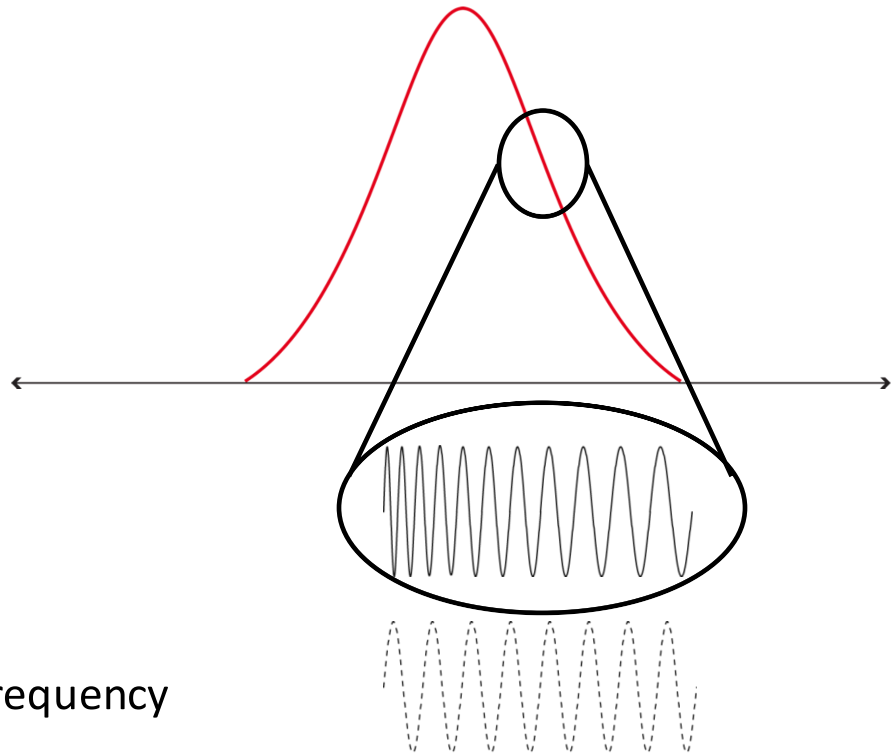


Third order non-linear optics example: Self-phase modulation

normal refractive index



time-dependent refractive index



$$w(t) = -\frac{dj\ (t)}{dt}$$; instantaneous frequency

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

The end.