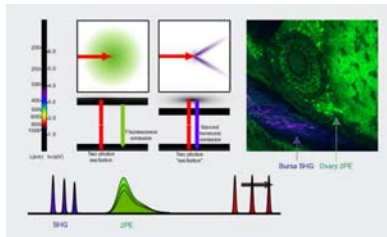


Phys 774: Nonlinear Spectroscopy: SHG and Raman Scattering

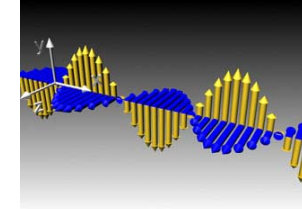


Fall 2007

1

Last Lectures: Polarization of Electromagnetic Waves

- ❖ General consideration of polarization
- ❖ Jones Formalism
- ❖ How Polarizers work
- ❖ Muller matrices
- ❖ Stokes parameters
- ❖ Poincare sphere



Polarization is important to understand nonlinear effects!

2

Broad field of nonlinear effects

- Optical Kerr effect, intensity dependent refractive index;
 - Self-focusing;
 - Kerr-lens modelocking (KLM).
 - Self-phase modulation (SPM), a $\chi^{(3)}$ effect.
 - Optical solitons.
 - Cross-phase modulation (XPM);
 - Four-wave mixing (FWM), can also arise from other nonlinearities.
 - Raman amplification,
 - Optical phase conjugation.
- Brillouin scattering, interaction of photons with acoustic phonons;
 - Optical phase conjugation.
- Two-photon absorption, simultaneous absorption of two photons, transferring the energy to a single electron;
- Multiple photoionisation, near-simultaneous removal of many bound electrons by one photon.
- Chaos in Optical Systems

We will consider in details only SHG and Raman Scattering

3

Linear vs. Nonlinear Spectroscopy

- ❖ Linear spectroscopy:

$$\vec{D} = \epsilon_0 \hat{\epsilon} \vec{E} = \epsilon_0 (1 + \hat{\chi}) \vec{E} = \epsilon_0 \vec{E} + \epsilon_0 \vec{P}$$

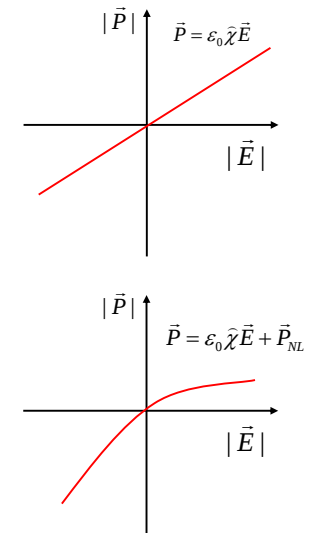
$$\begin{bmatrix} D_x \\ D_y \\ D_z \end{bmatrix} = \epsilon_0 \cdot \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad \vec{P} = \epsilon_0 \hat{\chi} \vec{E}$$

- ❖ Nonlinear effects:

$$\vec{P} = \epsilon_0 \hat{\chi} \vec{E} + \vec{P}_{NL}$$

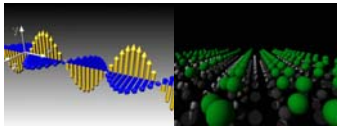
$$P_{NL} = \chi^{(2)} E^2$$

$$(\vec{P}_{NL})_i = 2d_{ijk} E_j E_k$$



Induced polarization vs. electric field in linear dielectric and in a crystal without center of inversion, where electrons move in asymmetric potential.

4

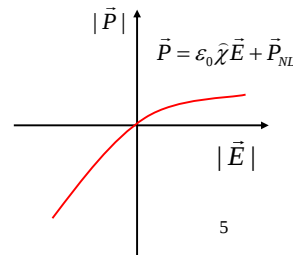
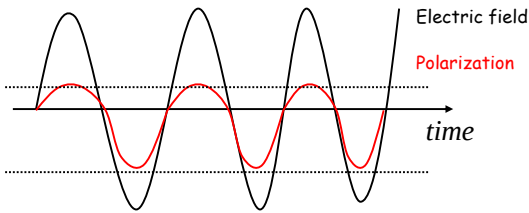
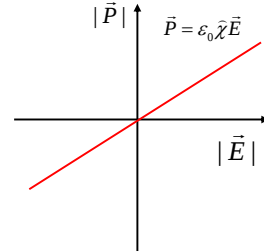
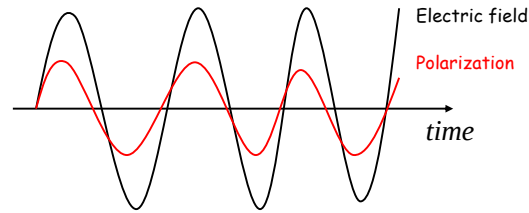


In vacuum

In a materials media

Electric field and Polarization

$$\vec{E}(r, t) = \vec{E}_0 \exp[i(\vec{k}\vec{r} - \omega t)]$$



5

Nonlinear polarization in crystals

with the center of inversion

$$x \rightarrow -x$$

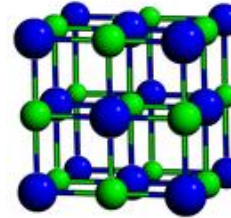
$$y \rightarrow -y$$

$$z \rightarrow -z$$

$$\hat{I} \cdot (\vec{P}_{NL})_i = (-\vec{P}_{NL})_i$$

$$\hat{I} \cdot (\vec{P}_{NL})_i = 2d_{ijk}(-E_j) \cdot (-E_k) = \vec{P}_{NL}$$

$$\vec{P}_{NL} = 0 \quad \text{or} \quad \hat{\chi}^{(2)} = d_{ijk} = 0$$



In general situation:

$$P_i = \epsilon_0 \chi_{ij} E_j + 2d_{ijk} E_j E_k + 4\chi_{ijkl}^{(3)} E_j E_k E_l +$$

In center-symmetric materials:

$$P_i = \epsilon_0 \chi_{ij} E_j + \cancel{2d_{ijk} E_j E_k} + 4\chi_{ijkl}^{(3)} E_j E_k E_l +$$

6

Microscopic understanding of nonlinearity

❖ Electronic contribution to susceptibility (linear response)

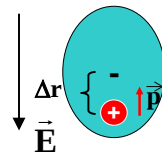
For simplicity consider one-dimensional case (Δr parallel to x)

Displaced electronic cloud feels a restoring force, which is linear (for small displacements)

$$\text{Total force } F = eE - \kappa \Delta r = m \frac{d^2 \Delta r}{dt^2}$$

κ = spring constant

m = mass



$$\text{Without an external field:} \quad -kx = m \frac{d^2 x}{dt^2}$$

Equation for harmonic oscillator. Solution: harmonic vibration

$$x(t) = x_0 e^{-i\omega_0 t} \quad \text{with frequency} \quad \omega_0 = \sqrt{k/m}$$

7

Now, have electromagnetic wave with field $E(t) = E_0 e^{-i\omega t}$

Force $F(t) = eE_0 e^{-i\omega t}$

Equation of motion becomes $eE_0 e^{-i\omega t} - m\omega_0^2 x = m \frac{d^2 x}{dt^2}$
(forced oscillator)

Look for a solution $x(t) = x_0 e^{-i\omega t}$ and get

$$x(t) = \frac{e/m}{\omega_0^2 - \omega^2} E_0 e^{-i\omega t} = \frac{e/m}{\omega_0^2 - \omega^2} E(t)$$

Expect strong response (large x), $\Rightarrow$ large susceptibility $\chi \Rightarrow$ large refractive index n at $\omega \approx \omega_0$

Dipole moment $p = qx$, so polarization $P = eNZx$

(N atoms per unit volume, Z electrons per atom) $\Rightarrow$

$$P = \frac{e^2 ZN}{\omega_0^2 - \omega^2} E \quad \text{Recall } P = \epsilon_0 \chi E \quad \text{and get} \quad \chi(\omega) = \frac{NZe^2}{\epsilon_0 m} \frac{1}{(\omega_0^2 - \omega^2)}$$

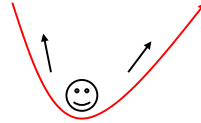
Linear response:

Microscopic understanding of nonlinearity

❖ Electronic contribution to susceptibility (nonlinear response)

Electron is moving in an asymmetric potential with damping

$$\frac{\partial^2 x(t)}{\partial t^2} + \gamma \frac{\partial x(t)}{\partial t} + \omega_0^2 x(t) + Dx^2(t) = \frac{e}{2m} E_0 e^{-i\omega t}$$



x – deviation from potential minimum

$mDx^2(t)$ Anharmonic restoring force

$\gamma \frac{\partial x(t)}{\partial t}$ Damping

Linear response:

Solution: $x(\omega, t) = (q_1 e^{-i\omega t} + q_2 e^{-i2\omega t})$

NonLinear response:
(second harmonic generation)

$$q_1 = \frac{eE_0}{m} \cdot \frac{1}{\omega_0^2 - \omega^2 + i\gamma \cdot \omega}$$

$$q_2 = \frac{-De^2 E_0^2}{2m^2 [\omega_0^2 - \omega^2 + i\gamma \cdot \omega]^2 [\omega_0^2 - (2\omega)^2 + i\gamma \cdot 2\omega]}$$

For NL polarization at the second harmonic frequency:

$$P^{2\omega} = Neq_2 e^{-i2\omega t} = \chi_{NL}^{(2)} \cdot E_0^2 e^{-i2\omega t}$$

For correct power consideration we need to take the complex conjugate part of the electromagnetic wave

$$P^{2\omega} = \frac{1}{2} Neq_2 (e^{-i2\omega t} + e^{+i2\omega t}) = \frac{1}{2} d_{NL} \cdot E_0^2 (e^{-i2\omega t} + e^{+i2\omega t})$$

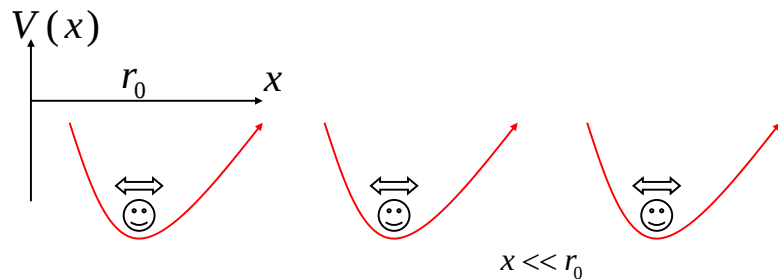
For nonlinear susceptibility we have:

$$\chi_{NL}^{(2)} = \frac{mD(\chi_L(\omega))^2 \cdot \chi_L(2\omega) \cdot \epsilon_0^3}{2N^2 |e^3|} \quad D \approx \frac{-3e^2}{\epsilon_0 m r_0^4}; \quad r_0 \approx 0.5 \text{ nm}$$

Why nonlinear effects are weaker than linear effects?

10

Why nonlinear effects are usually weaker than linear ones?



$$V(x) = \frac{m}{2} x^2 + \frac{m}{3} Dx^3 = \frac{e^2}{4\pi\epsilon_0} \left(\frac{-5.83}{r_0} + 24.1 \frac{x^2}{r_0^2} - 13.3 \frac{x^3}{r_0^3} + \dots \right)$$

11

Symmetry of nonlinear susceptibility tensor

$$|\vec{P}_{NL}| = \hat{\chi}^{(2)} \cdot |\vec{E}_1 \cdot \vec{E}_2|$$

$$(\vec{P}_{NL})_i = 2d_{ijk} E_j E_k$$

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \cdot \begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_z E_y \\ 2E_z E_x \\ 2E_x E_y \end{bmatrix}$$

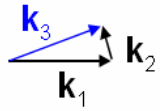
For cubic, tetragonal, and orthorhombic crystals:

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & d' & 0 & 0 \\ 0 & 0 & 0 & 0 & d' & 0 \\ 0 & 0 & 0 & 0 & 0 & d'' \end{bmatrix}$$

12

Two-wave mixing

General case of two-wave mixing:



$$\omega_1 + \omega_2 = \omega_3$$

$$(\omega_3 = \omega_1 + \omega_2)$$

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$

Wave equation for linear process: $\nabla^2 \vec{E} = \epsilon \mu \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \mu \frac{\partial \vec{E}}{\partial t}$

Wave equation for nonlinear process: $\nabla^2 \vec{E} = \epsilon \mu \frac{\partial^2 \vec{E}}{\partial t^2} + \sigma \mu \frac{\partial \vec{E}}{\partial t} + \mu \frac{\partial^2 \vec{P}_{NL}}{\partial t^2}$

Wave propagation along z ;

i, j, k index are permutations of x and y coordinates

$$\frac{dE_{1i}}{dz} = -\frac{\sigma_1}{2} \sqrt{\frac{\mu}{\epsilon_1}} E_{1i} - i\omega_1 \sqrt{\frac{\mu}{\epsilon_1}} d'_{ijk} E_{3j} E_{2k}^* e^{-i(k_3 - k_2 - k_1)z}$$

$$\frac{dE_{2k}^*}{dz} = -\frac{\sigma_2}{2} \sqrt{\frac{\mu}{\epsilon_2}} E_{2k}^* - i\omega_2 \sqrt{\frac{\mu}{\epsilon_2}} d'_{ijk} E_{1i} E_{3j} e^{-i(-k_3 + k_2 + k_1)z}$$

$$\frac{dE_{3j}}{dz} = -\frac{\sigma_3}{2} \sqrt{\frac{\mu}{\epsilon_3}} E_{3j} - i\omega_3 \sqrt{\frac{\mu}{\epsilon_3}} d'_{ijk} E_{1i} E_{2k} e^{-i(-k_3 + k_2 + k_1)z}$$

13

Second-harmonic generation

SHG: $\omega + \omega = 2\omega$ ($\omega_3 = 2\omega_1$) $\frac{dE_{1i}}{dz} \approx 0$ Small loss of power in the primary beam

$$2\vec{k}_\omega = \vec{k}_{2\omega}$$

$$\frac{dE_{3j}}{dz} = -i2\omega \sqrt{\frac{\mu}{\epsilon}} d'_{ijk} E_{1i} E_{1k} e^{-i\Delta k z}$$

$$E_{3j}(z) = -i2\omega \sqrt{\frac{\mu}{\epsilon}} d'_{ijk} E_{1i} E_{1k} \frac{e^{-i\Delta k z} - 1}{i\Delta k}$$

$$\text{Power}(2\omega) = E_{3j}(L) E_{3j}^*(L) = 4 \frac{\mu}{\epsilon_3} \omega^2 (d'_{ijk})^2 E_{1i}^2 E_{1k}^2 \frac{\sin^2(\Delta k L / 2)}{(\Delta k L / 2)^2}$$

Coherence length: $l = \frac{2\pi}{\Delta k}$

Phase matching requirement:

$$2|\vec{k}_\omega| = 2\tilde{n}(\omega) \frac{\omega}{c} = \tilde{n}(\omega) \frac{2\omega}{c}$$

$$\Delta n = n_e - n_o$$

$$\hat{\epsilon} = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} = \begin{bmatrix} n_e^2 & 0 & 0 \\ 0 & n_o^2 & 0 \\ 0 & 0 & n_o^2 \end{bmatrix}$$

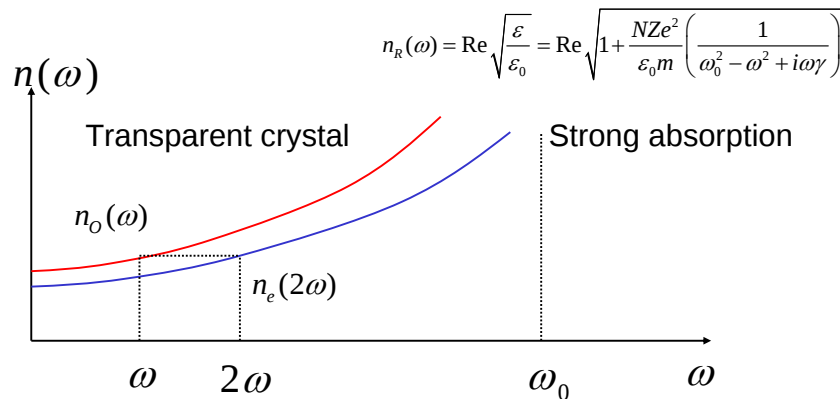
$$|\vec{k}_{2\omega}| = \tilde{n}(2\omega) \frac{2\omega}{c}$$

$$\tilde{n}(\omega) \neq \tilde{n}(2\omega) !$$

If in birefringent crystal $n_e(2\omega) = n_o(\omega) \Rightarrow 2\vec{k}_\omega = \vec{k}_{2\omega}$ 14

Second-harmonic generation

If in birefringent crystal $n_e(2\omega) = n_o(\omega) \Rightarrow 2\vec{k}_\omega = \vec{k}_{2\omega}$



Blue waves propagate with the same velocity in the crystal

15

Experimental setup for Second-harmonic generation

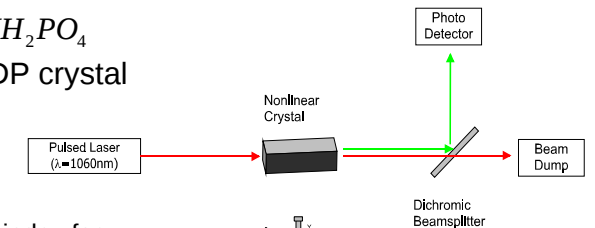
$$\omega + \omega = 2\omega$$

KH_2PO_4

$$2\vec{k}_\omega = \vec{k}_{2\omega}$$

KDP crystal

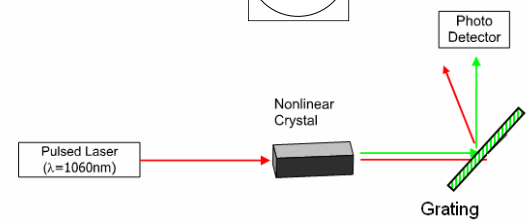
$$n_e(2\omega) = n_o(\omega)$$



Fine tuning of refractive index for Phase matching in uniaxial Nonlinear crystals:

$$\frac{1}{n(\theta)^2} = \frac{\cos \theta}{n_o^2} + \frac{\sin \theta}{n_e^2}$$

$$\hat{\epsilon} = \begin{bmatrix} n_e^2 & 0 & 0 \\ 0 & n_o^2 & 0 \\ 0 & 0 & n_o^2 \end{bmatrix}$$



16

Applications of Second-harmonic generation

- ❖ Lasers (Nd:YAG, second harmonic)
- ❖ Coherent anti-Stokes Raman scattering
- ❖ Bio-imaging
- ❖ Materials Physics
- ❖ Solar Physics
- ❖ Quantum cryptography (two-wave mixing)

Common SHG materials

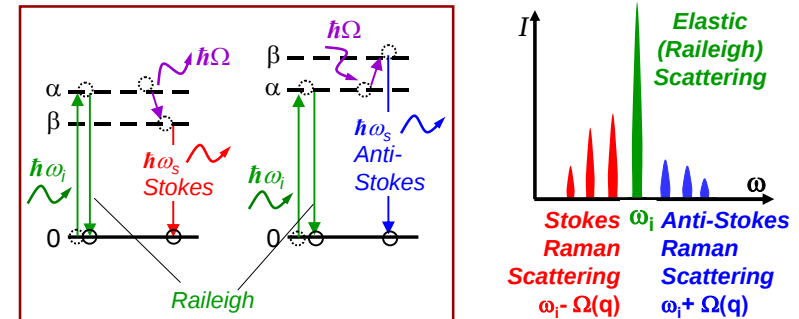
- 806 nm light : lithium iodate (LiIO_3)
- 860 nm light : potassium niobate (KNbO_3)
- 980 nm light : KNbO_3
- 1064 nm light : monopotassium phosphate (KH_2PO_4 , KDP), lithium triborate (LBO) and β -barium borate (BBO).
- 1319 nm light : KNbO_3 , BBO, KDP, potassium titanyl phosphate (KTP), lithium niobate (LiNbO_3), LiIO_3 , and Ammonium Dihydrogen Phosphate (ADP)

17

Brillouin and Raman spectroscopy

Inelastic light scattering mediated by the *electronic polarizability* of the medium

- a material or a molecule scatters irradiant light from a source
- Most of the scattered light is at the same wavelength as the laser source (elastic, or *Raileigh scattering*)
- but a small amount of light is scattered at different wavelengths (inelastic, or *Raman scattering*)



Analysis of scattered light energy, polarization, relative intensity provides information on lattice vibrations or other excitations¹⁸

Raman scattering in crystalline solids

Not every crystal lattice vibration can be probed by Raman scattering. There are certain **Selection rules**:

1. Energy conservation:

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\Omega;$$

2. Momentum conservation:

$$\mathbf{k}_i = \mathbf{k}_s \pm \mathbf{q} \Rightarrow 0 \leq |\mathbf{q}| \leq 2|\mathbf{k}| \Rightarrow 0 \leq |q| \leq \frac{4\pi m}{\lambda_i}$$

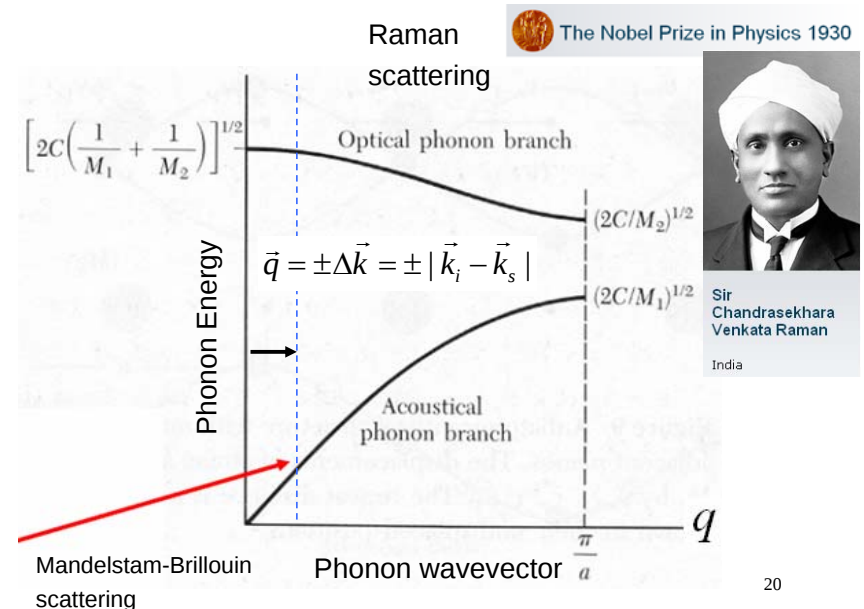
$$\lambda_i \sim 5000 \text{ \AA}, a_0 \sim 4\text{-}5 \text{ \AA} \Rightarrow \lambda_{\text{phonon}} \gg a_0$$

$\Rightarrow$ only small wavevector (close to BZ center) phonons are seen in the 1st order (single phonon) Raman spectra of bulk crystals

3. Selection rules determined by crystal symmetry

19

Raman scattering in crystalline solids



20