Nonlinear optics with metals

Martti Kauranen

Department of Physics

Tampere University of Technology

Finland

Where is Tampere?

Optics in Tampere

- Tampere University of Technology
  - Department of **Physics** (applied optics, nonlinear optics)
  - **ORC** (semiconductors, ultrafast optics, nanostructured materials)
  - Department of **Chemistry** (photochemistry)
- Spinoff companies
  - **Coherent** (diode lasers)
  - **Modulight** (diode lasers)
  - **Liekki** (nanoparticle doped optical fibers)
  - **Corelase** (fiber lasers for materials processing)
  - **Cavitar** (pulsed illumination and visualization)
  - **Oseir** (industrial imaging)
  - **Epicrystals** (laser sources for projection displays)
  - **Reflekron** (customized SESAMs)

Acknowledgments

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  - several students and postdocs over several years
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- **University of Eastern Finland**
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  - Finnish Funding Agency for Technology and Innovation
  - Ministry of Education of Finland (Research and Technology Program on Nanophotonics)

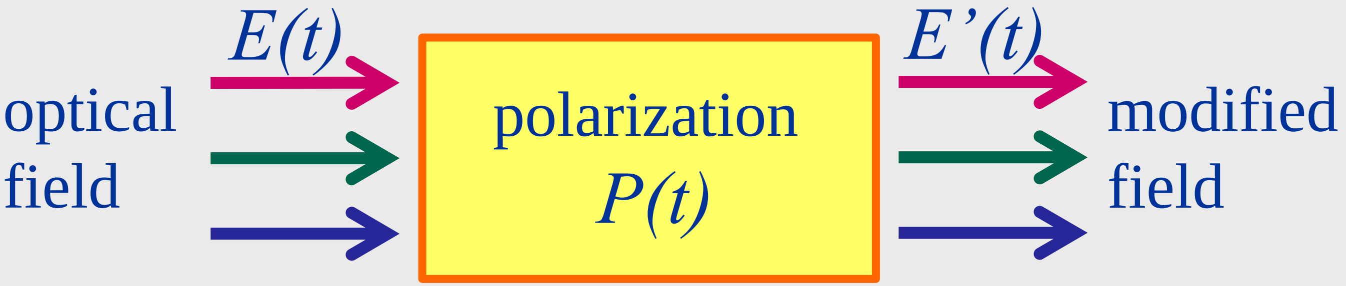
Outline

- **Part I: Multipole Effects in Nonlinear Optics**
  - electric-dipole and higher-multipole nonlinearities
  - surface and bulk effects

- **Part II: Second-Order Response of Nanoscale Metals**
  - higher-multipole radiation
  - local-field effects

- **Part III: Present challenges**
  - tailorable nonlinear response
  - surface vs. bulk origin of metal nonlinearity
  - towards metamaterials with optimized nonlinear response

Optical response of materials



oscillating field → **oscillating polarization**

→ **radiation** → **modified field**

- **Optical field** $E(t) = E_\omega e^{-i\omega t} + c.c.$
- **Linear optics**

$$\boxed{P(t) = \chi^{(1)} E(t) = \chi^{(1)} E_\omega e^{-i\omega t}}$$

Nonlinear optics

- **Material polarization**

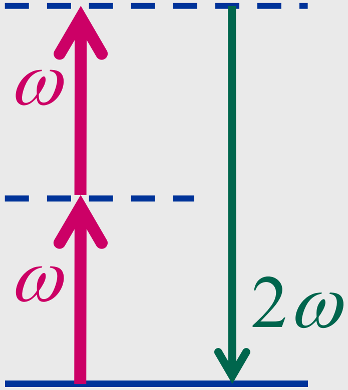
$$E(t) = E_\omega e^{-i\omega t}$$

$$P(t) = \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \ldots$$

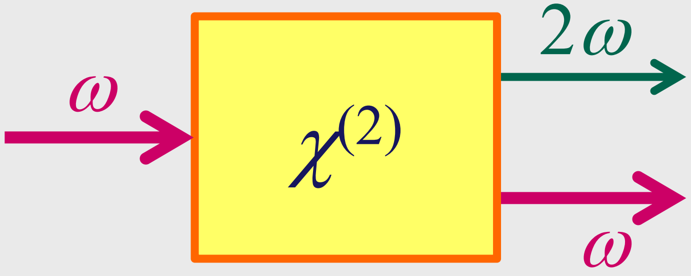
- **Second order**

$$\boxed{P(t) = \chi^{(2)} E^2(t) = \chi^{(2)} E_\omega^2 e^{-i2\omega t}}$$

➡ **second-harmonic generation**



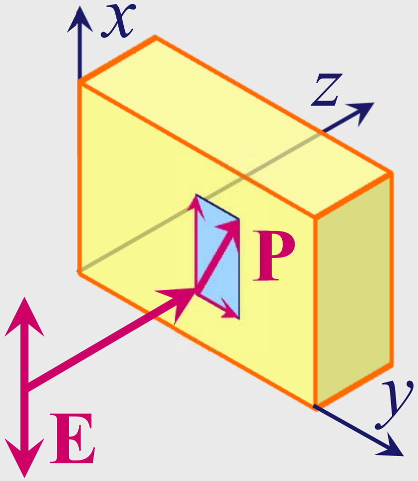
- **Third order**
  - third harmonic
  - original frequency



Tensorial responses

- Vector quantities **E** **P**
- Linear response

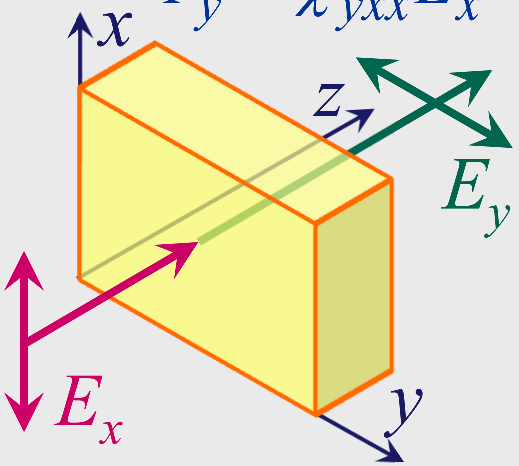
$$P_i = \sum_j \chi_{ij}^{(1)} E_j \qquad \mathbf{P} = \boldsymbol{\chi}^{(1)} \bullet \mathbf{E}$$



- Second-order response

$$P_i = \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k \qquad \mathbf{P} = \boldsymbol{\chi}^{(2)} : \mathbf{EE}$$

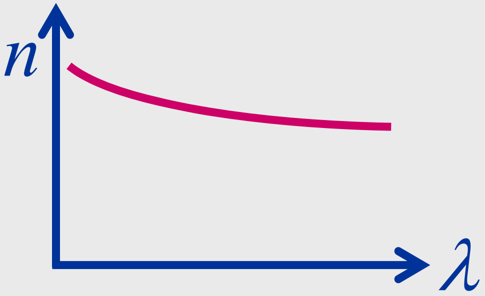
$$P_y = \chi_{yxx}^{(2)} E_x^2$$



polarization dependent
optical responses

Dispersion and permutation

- **Dispersion**
  - response depends on wavelength
  - resonance enhancement
  - frequency-dependent susceptibility



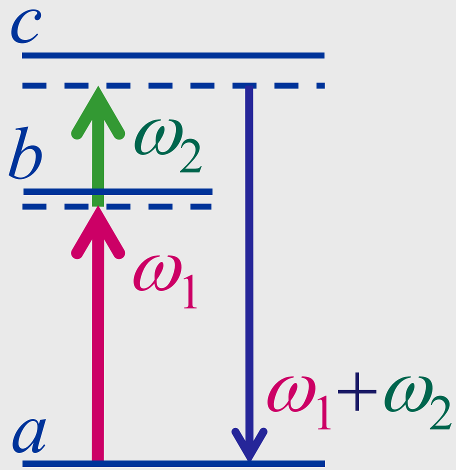
$$\chi^{(2)}_{ijk}(\omega_1+\omega_2;\omega_1,\omega_2)\sim\frac{1}{(\omega_{ca}-\omega_1-\omega_2)(\omega_{ba}-\omega_1)}+\ldots$$

- **Permutation symmetry**

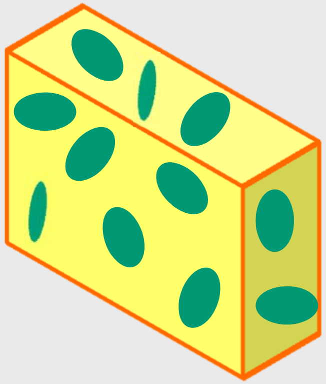
$$\chi^{(2)}_{ikj}(\omega_1+\omega_2;\omega_1,\omega_2)=\chi^{(2)}_{ijk}(\omega_1+\omega_2;\omega_2,\omega_1)$$

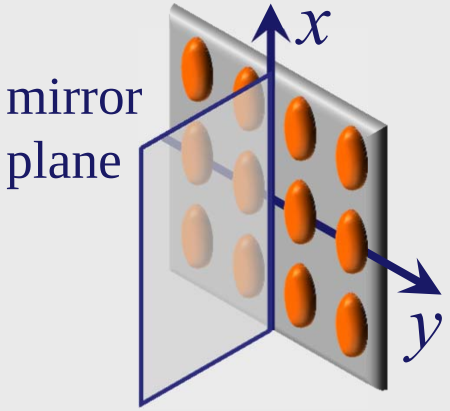
SHG

$$\chi^{(2)}_{ikj}(2\omega;\omega,\omega)=\chi^{(2)}_{ijk}(2\omega;\omega,\omega)$$



Symmetry issues



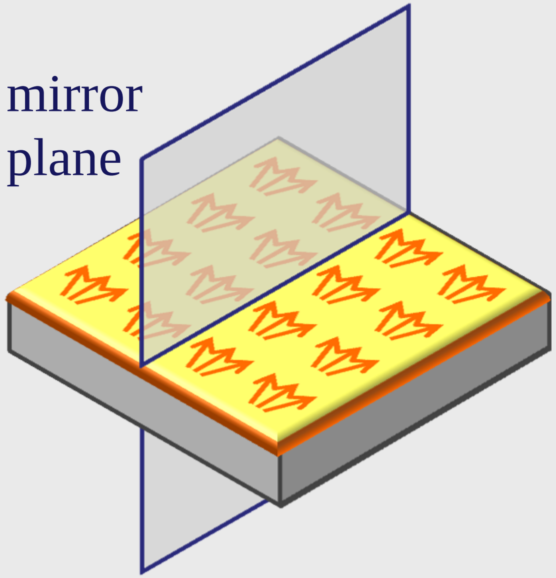


- **Spatial symmetry**
  - symmetry group of material
- **Linear response**
  - isotropic achiral material

    → **no polarization dependence**
  - anisotropic material

    → **birefringence**
- **Nonlinear response**
  - interdependent tensor components

    → $\chi^{(2)}_{ijk} \neq 0 \quad \chi^{(2)}_{ijk} = C\chi^{(2)}_{lmn}$

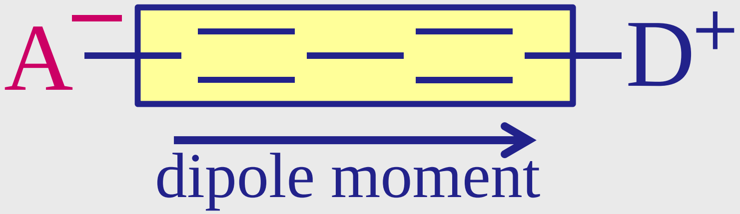


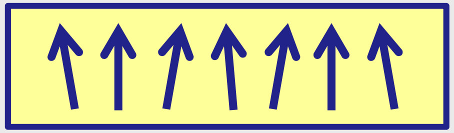
Centrosymmetry

- **Inversion** $\mathbf{r} \rightarrow -\mathbf{r} \quad \mathbf{E} \rightarrow -\mathbf{E} \quad \mathbf{P} \rightarrow -\mathbf{P}$

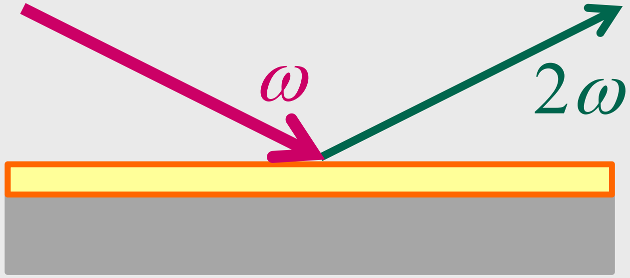
$$-\mathbf{P} = \chi^{(2)} : (-\mathbf{E})^2 = \chi^{(2)} : \mathbf{E}^2 = \mathbf{P} \Longrightarrow \boxed{\chi^{(2)} = 0}$$

- **Second-order materials**
  - noncentrosymmetric units
  - noncentrosymmetric ordering
  - traditionally polar order

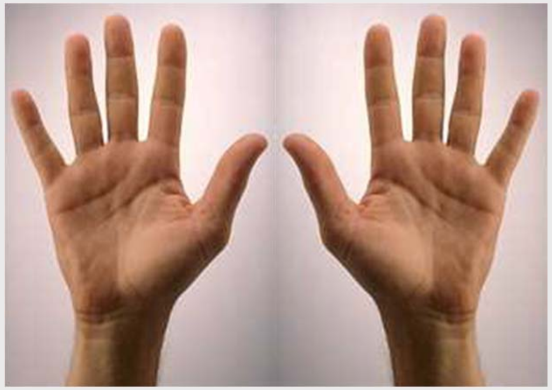




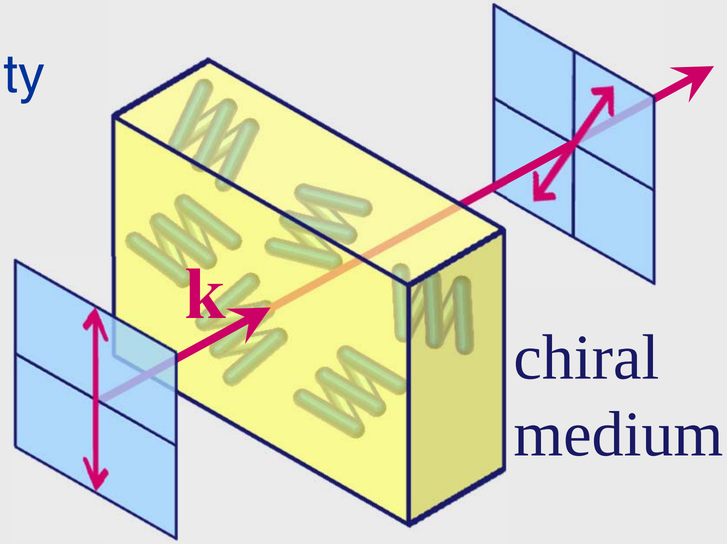
- **Surface and thin films**
  - centrosymmetry broken
  - probes based on SHG and SFG



Optical activity



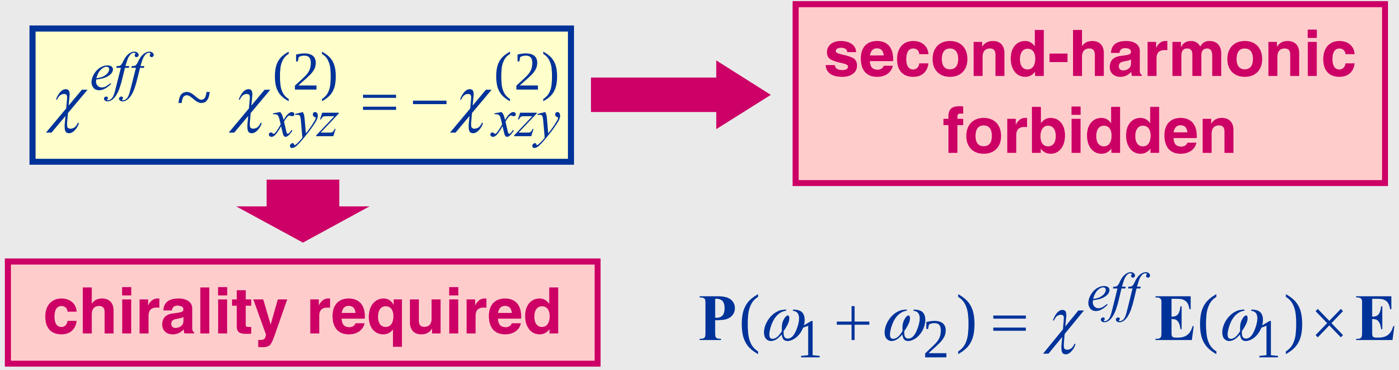
- **Chiral objects**
  - lack of reflection symmetry
  - cannot be superimposed on its mirror image
  - occur in two mirror-image forms (enantiomers)
- **Optical activity**
  - optical effects associated with chirality
  - different response to circular eigenpolarizations
  - polarization rotation
  - circular dichroism
  - reverse sign between the enantiomers



Isotropic materials

- **Electric-dipole response**
  - effective susceptibility

$$\boxed{\chi^{eff} \sim \chi^{(2)}_{xyz} = -\chi^{(2)}_{xzy}}$$

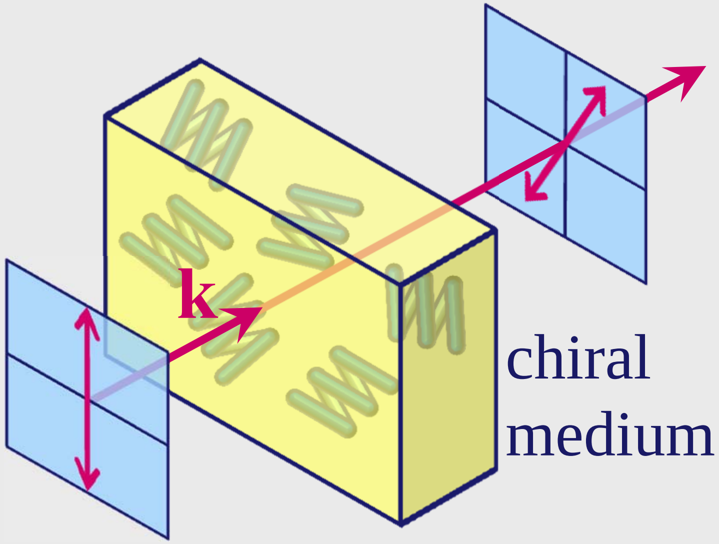


second-harmonic forbidden

chirality required

$$\mathbf{P}(\omega_1+\omega_2) = \chi^{eff}\,\mathbf{E}(\omega_1)\times\mathbf{E}(\omega_2)$$

- **Sum-frequency generation**
  - arabinose solution (Rentzepis 1966)
  - recently reinvestigated

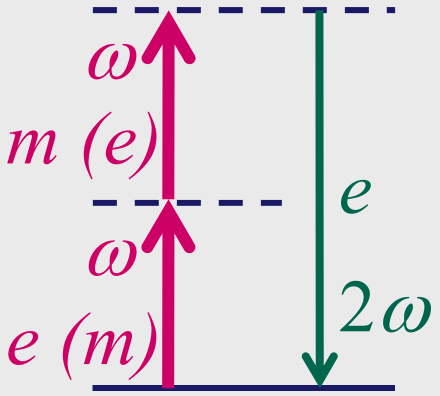


Multipole interactions

- **Hamiltonian** $H = -\boldsymbol{\mu}\cdot\mathbf{E} - \boxed{\mathbf{m}\cdot\mathbf{B} - \mathbf{Q}:\nabla\mathbf{E} + \cdots}$ **weak**

- **Linear response**

$$\boxed{\begin{array}{ll} \mathbf{P}_{\omega} = \boldsymbol{\chi}^{ee}\cdot\mathbf{E}_{\omega} + \boldsymbol{\chi}^{em}\cdot\mathbf{B}_{\omega} + \boldsymbol{\chi}^{eQ}:\nabla\mathbf{E}_{\omega} & \\ \mathbf{M}_{\omega} = \boldsymbol{\chi}^{me}\cdot\mathbf{E}_{\omega} \qquad \mathbf{Q}_{\omega} = \boldsymbol{\chi}^{Qe}\cdot\mathbf{E}_{\omega} & \end{array}}$$



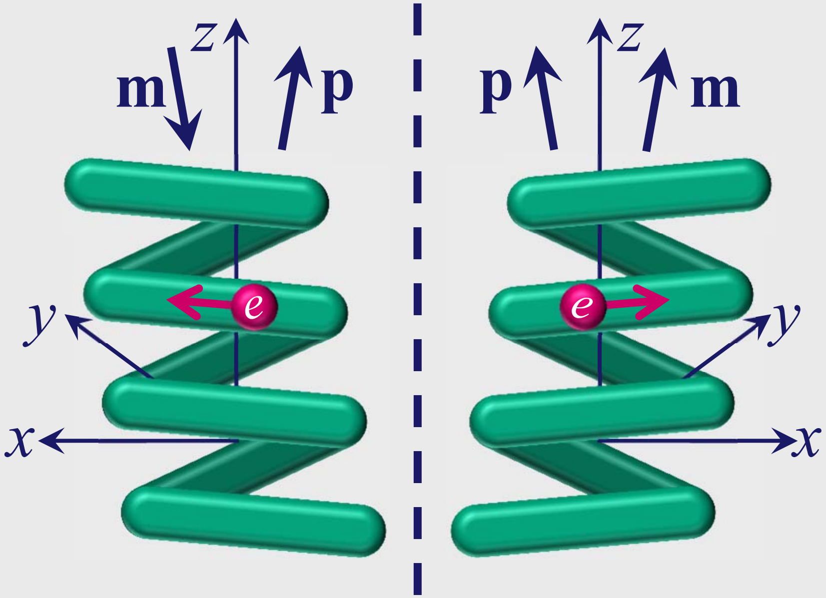
- **Second-order response**

$$\boxed{\begin{array}{l} \mathbf{P}_{2\omega} = \boldsymbol{\chi}^{eee}:\mathbf{E}_{\omega}\mathbf{E}_{\omega} + \boldsymbol{\chi}^{eem}:\mathbf{E}_{\omega}\mathbf{B}_{\omega} + \boldsymbol{\chi}^{eeQ}\vdots\mathbf{E}_{\omega}\nabla\mathbf{E}_{\omega} \\ \mathbf{M}_{2\omega} = \boldsymbol{\chi}^{mee}:\mathbf{E}_{\omega}\mathbf{E}_{\omega} \qquad \mathbf{Q}_{2\omega} = \boldsymbol{\chi}^{Qee}:\mathbf{E}_{\omega}\mathbf{E}_{\omega} \end{array}}$$

Electric and magnetic quantities

- **Proper transformations**
  - rotations
- **Polar vectors**
  - transform as **r**
- **Electric quantities**
  - polar vectors
  - odd under parity
  - even under time reversal
- **Magnetic quantities**
  - axial vectors
  - even under parity
  - odd under time reversal

- **Improper transformations**
  - reflections, inversion
- **Axial vectors**
  - transform opposite to **r** under improper transformations



reflection plane

Multipole symmetries

- **Second-harmonic generation**

$$\boxed{P_i = \chi^{eee}_{ijk} E_j E_k + \chi^{eem}_{ijk} E_j \underset{\substack{\uparrow\\ \text{axial}}}{B_k} + \chi^{eeQ}_{\underset{\substack{\uparrow\\ \text{4th rank}}}{ijkl}} E_j \nabla_k E_l}$$

- **Magnetic and quadrupole tensors**
  - symmetry properties are different from those of the electric-dipole tensor

→ **electric-dipole-forbidden effects can occur**

Isotropic material

- **Third-rank tensors**
  - full rotational symmetry

$$\chi_{xyz} = \chi_{yzx} = \chi_{zxy} = -\chi_{xzy} = -\chi_{yxz} = -\chi_{zyx}$$

  - permutation symmetry
  - centrosymmetry

SHG

$$\chi^{eee} = 0 \qquad \chi^{mee} = 0$$

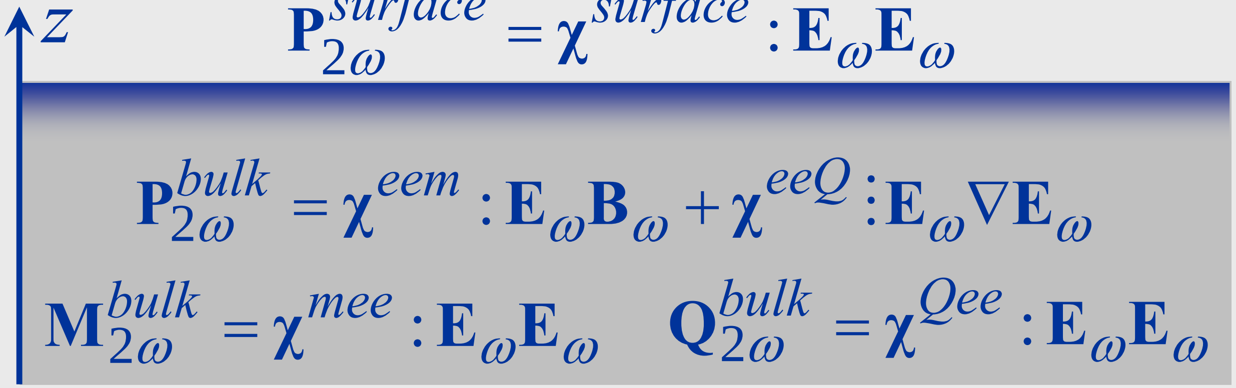
$$\chi^{eem} \neq 0$$

- **Fourth-rank tensors**
  - full rotational symmetry
  - centrosymmetry

$$\chi_{iijj} \neq 0, \ \chi_{ijij} \neq 0, \ \chi_{ijji} \neq 0$$

$$\chi_{iiii} = \chi_{iijj} + \chi_{ijij} + \chi_{ijji}$$

Surface and bulk contributions



$$\mathbf{P}_{2\omega}^{surface} = \boldsymbol{\chi}^{surface} : \mathbf{E}_{\omega}\mathbf{E}_{\omega}$$

$$\mathbf{P}_{2\omega}^{bulk} = \boldsymbol{\chi}^{eem} : \mathbf{E}_{\omega}\mathbf{B}_{\omega} + \boldsymbol{\chi}^{eeQ} : \mathbf{E}_{\omega}\nabla\mathbf{E}_{\omega}$$

$$\mathbf{M}_{2\omega}^{bulk} = \boldsymbol{\chi}^{mee} : \mathbf{E}_{\omega}\mathbf{E}_{\omega} \qquad \mathbf{Q}_{2\omega}^{bulk} = \boldsymbol{\chi}^{Qee} : \mathbf{E}_{\omega}\mathbf{E}_{\omega}$$

- **Surface**
  - electric-dipole and higher-multipole response
  - behaves as effective electric-dipole response
- **Bulk**
  - magnetic and quadrupole response
  - effective polarization

$$\boxed{\mathbf{P}_{2\omega}^{eff} = \mathbf{P}_{2\omega} - \nabla \cdot \mathbf{Q}_{2\omega} + i(c/2\omega)\nabla \times \mathbf{M}_{2\omega}}$$

Isotropic material

- **Effective bulk polarization**

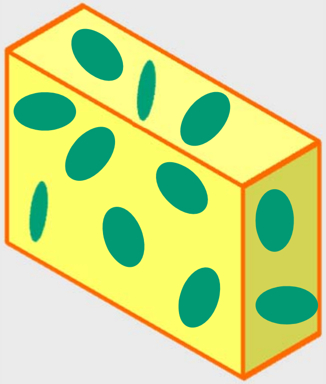
$$\mathbf{P}_{2\omega}^{bulk} = \beta \mathbf{E}_{\omega}(\nabla \cdot \mathbf{E}_{\omega}) + \gamma \nabla(\mathbf{E}_{\omega} \cdot \mathbf{E}_{\omega}) + \delta '(\mathbf{E}_{\omega} \cdot \nabla)\mathbf{E}_{\omega}$$

- **Bulk parameters**

$$\beta = \chi_{xxyy}^{eeQ} - \chi_{xyyx}^{Qee} - \chi_{xyxy}^{Qee}$$

$$\gamma = \chi_{xyyx}^{eeQ} / 2 - \chi_{xxyy}^{Qee} - (ic / 2\omega)\chi_{xyz}^{eem}$$

$$\delta ' = \chi_{xyyx}^{eeQ} - 2\chi_{xyxy}^{Qee} + (ic / \omega)\chi_{xyz}^{eem}$$



Progress in Optics **51**, 69 (2008)

Isotropic material

- **Effective bulk polarization**

$$\boxed{\mathbf{P}_{2\omega}^{bulk} = \beta\mathbf{E}_\omega(\nabla\cdot\mathbf{E}_\omega) + \gamma\nabla(\mathbf{E}_\omega\cdot\mathbf{E}_\omega) + \delta'(\mathbf{E}_\omega\cdot\nabla)\mathbf{E}_\omega}$$

$$\nabla\cdot\mathbf{E}_\omega = 0$$

$$\chi^{surface}$$

separable bulk contribution

- **Surface**
  - effective electric-dipole tensor

$$\boxed{\boldsymbol{\chi}^{s} = \boldsymbol{\chi}^{s,dipolar} + \boldsymbol{\chi}^{s,multipolar}}$$

  - isotropic surface symmetry

→ **measurable components**

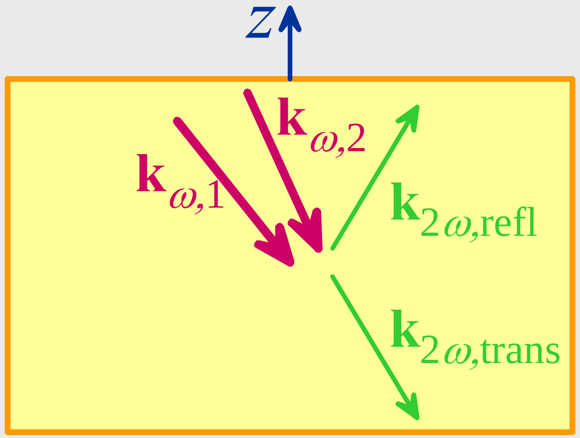
$$\begin{aligned}\chi_{zzz}^{s,eff} &= \chi_{zzz}^{s} + \gamma\\ \chi_{zxx}^{s,eff} &= \chi_{zxx}^{s} + \gamma\\ \chi_{xxz}^{s,eff} &= \chi_{xxz}^{s}\end{aligned}$$

Separable bulk contribution

$$\boxed{\mathbf{P}_{2\omega}^{bulk} = \delta'(\mathbf{E}_\omega \cdot \nabla)\mathbf{E}_\omega}$$

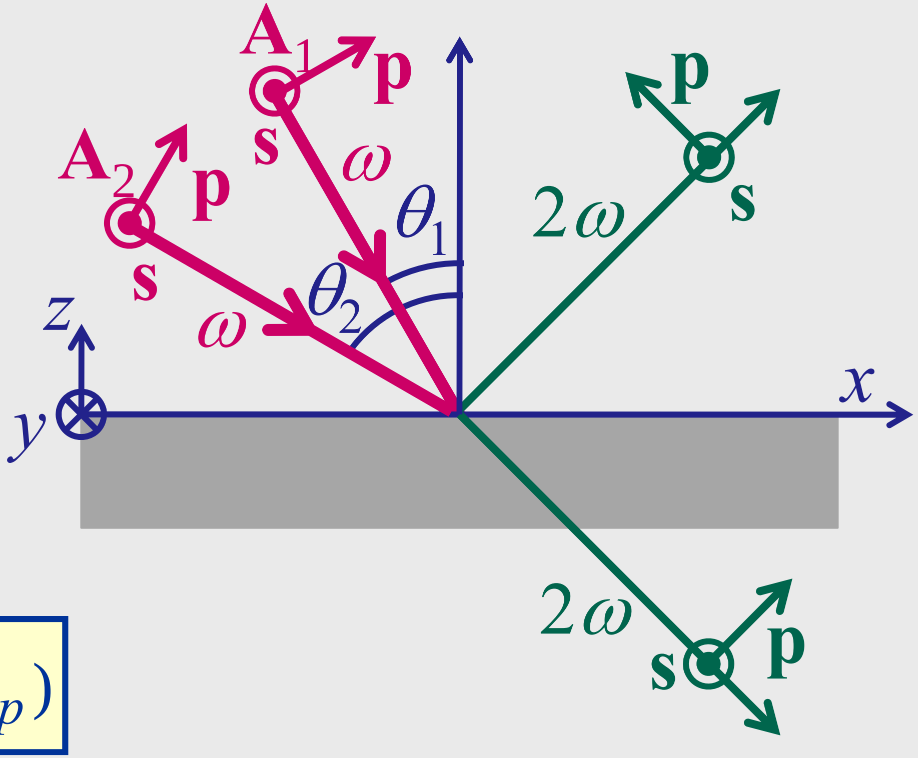
- **Effective polarization**
  - two input beams required
  - coherent growth in the bulk

$$L_c \sim \frac{1}{\left|\mathbf{k}_{2\omega} - (\mathbf{k}_{\omega,1} + \mathbf{k}_{\omega,1})\right|}$$



- **Separation** (Shen 1980’s – 2000’s)
  - different bulk and surface spectra in SFG
  - different coherence lengths in reflection and transmission
  - difficult due to dispersion and calibration problems

Polarization signatures



- **s-polarized signals**
  - unique signatures
  - not sensitive to linear optics

- **Isotropic bulk**

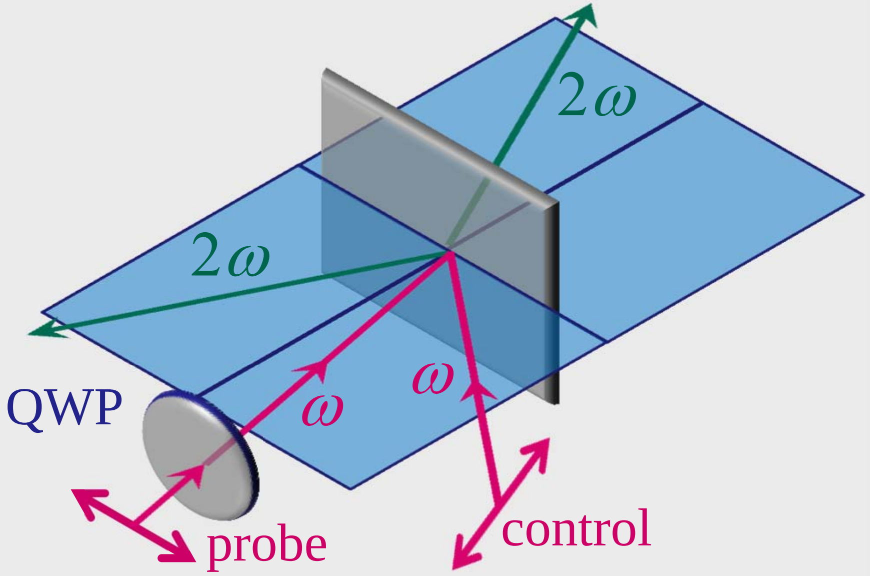
$$\boxed{A_{2\omega}^{bulk} \propto \delta'(A_{1p}A_{2s} - A_{1s}A_{2p})}$$

- **Isotropic surface**

$$\boxed{A_{2\omega}^{surface} \propto \chi_{yyz}^{surface}(A_{1p}A_{2s} + \frac{\sin\theta_2}{\sin\theta_1}A_{1s}A_{2p})}$$

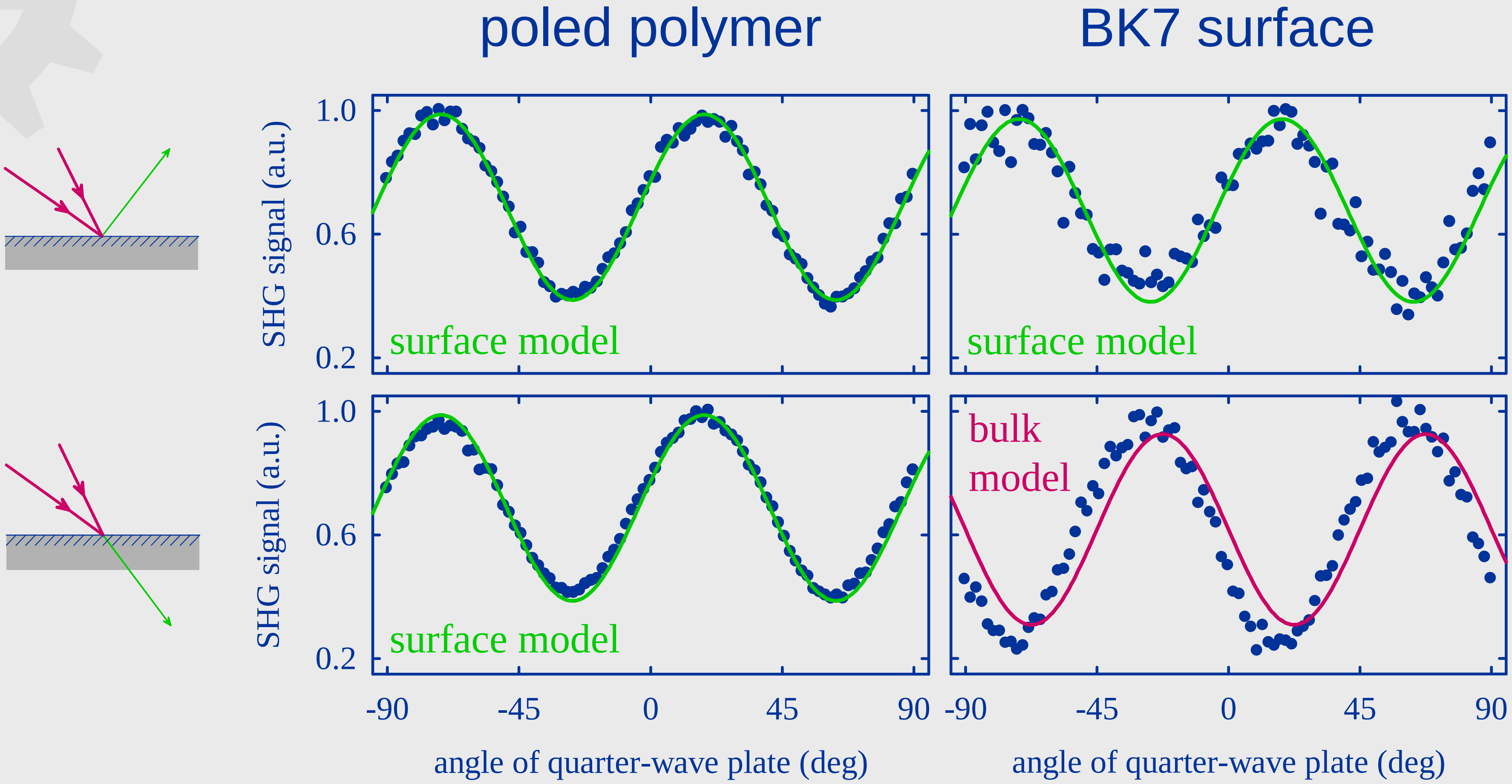
PRB **72**, 033412 (2005)

Experiment: Two-beam SHG



- **Control beam**
  - polarization fixed
- **Probe beam**
  - polarization varied
- **SHG signals**
  - reflected and transmitted
- **Samples**
  - poled polymer film → surface dominates
  - BK7 glass → surface-bulk competition?

Results for BK7

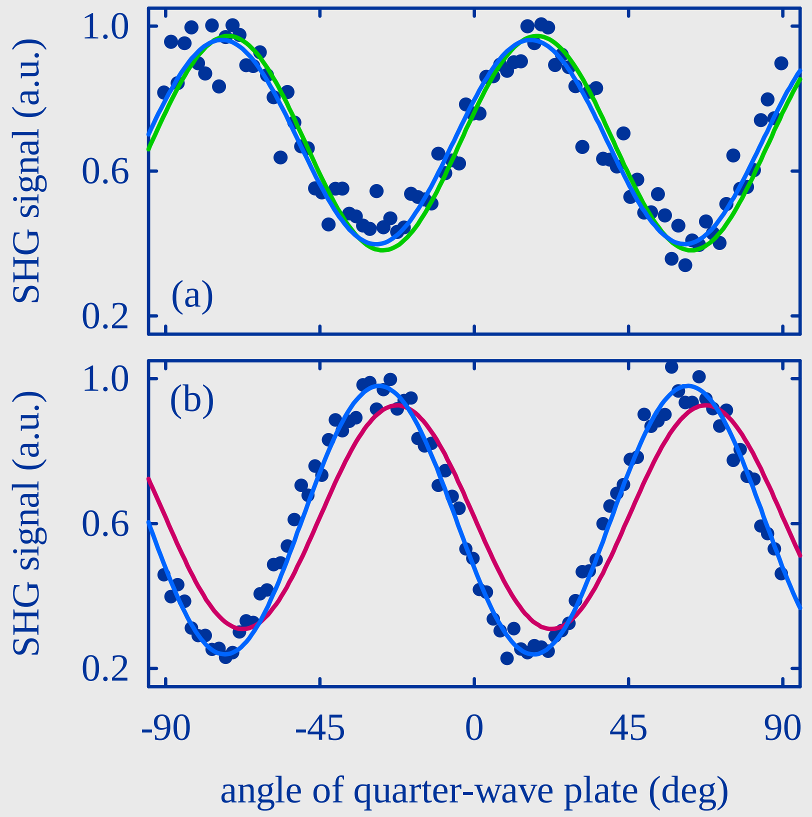


PRB **72**, 033412 (2005)

Detailed analysis of BK7

- **Surface-bulk interference**

$$A_{2\omega} = A_{2\omega}^{surface} + SA_{2\omega}^{bulk}$$



reflection $L_c = 0.12\,\mu\text{m}$

surface only

surface+bulk $S = -0.08$

transmission $L_c = 10\,\mu\text{m}$

bulk only

surface+bulk $S = 6.54$

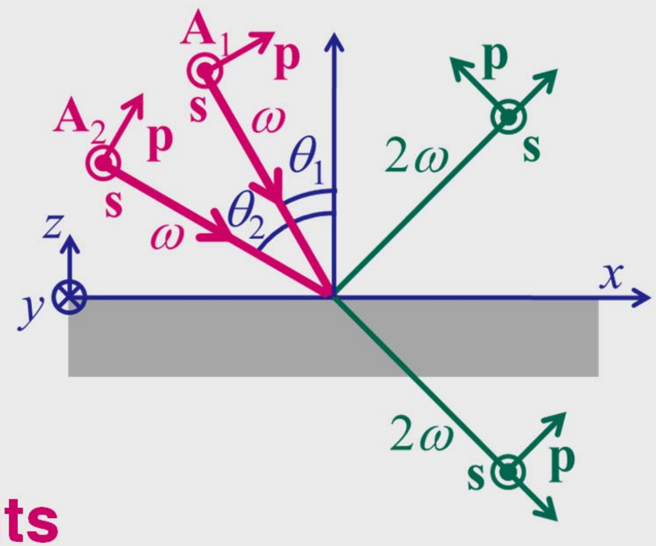
bulk contribution scales with coherence length

Complete polarization study

- **Isotropy**

$$\boxed{A_{2\omega,s} = f_{sps} A_{1p} A_{2s} + f_{ssp} A_{1s} A_{2p}}$$

$$\boxed{A_{2\omega,p} = f_{ppp} A_{1p} A_{2p} + f_{pss} A_{1s} A_{2s}}$$



- **Detailed polarization measurements**
  - unique expansion coefficients

$$f_{ijk} = f_{ijk}(\chi_{zzz}^{s,eff}, \chi_{zxx}^{s,eff}, \chi_{xxz}^{s,eff}, \delta')$$

➡ **solve tensor components**

Tensor analysis of BK7 glass

- **Effective surface components**

$$\boxed{\begin{aligned}
\chi_{zzz}^{s,eff} &= \chi_{zzz}^{s,dipolar} + \chi_{zzz}^{s,multipolar} + \gamma = 6.4\\
\chi_{zxx}^{s,eff} &= \chi_{zxx}^{s,dipolar} + \chi_{zxx}^{s,multipolar} + \gamma = 0.49\\
\chi_{xxz}^{s,eff} &= \chi_{xxz}^{s,dipolar} + \chi_{xxz}^{s,multipolar} = 1
\end{aligned}}$$

- **Separable bulk contribution**

$$\boxed{\delta' = 1.01}$$

- **Calibration against quartz**

Opt. Express **15**, 8695 (2007)
Opt. Express **16**, 8704 (2008)

Summary

- **Material symmetry**
  - strong influence on second-order nonlinear properties
  - electric-dipole and higher-multipole effects
  - polarization effects
- **Surface and bulk contributions**
  - unambiguous separation by two-beam SHG
  - magnetic effects important in the bulk of glasses
- **Future work**
  - models with various multipoles explicit
  - materials with enhanced multipolar responses