Nonlinear optics with metals

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Outline

- **Part I: Multipolar Symmetries in Second-Order Nonlinear Optics**
  - electric-dipole and higher-multipole nonlinearities
  - isotropic and centrosymmetric materials
  - separation of surface and bulk effects
- **Part II: Second-Order Nonlinear Optical Response of Nanoscale Metals**
  - effective multipoles
  - local-field effects
  - higher multipole radiation
  - origin of metal nonlinearity
  - separation of surface and bulk effects

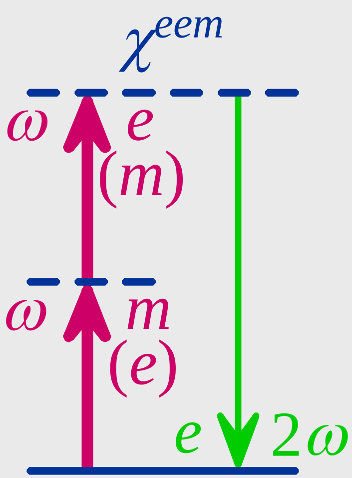
Multipole interactions

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

- **Linear response**

$$\mathbf{P}_\omega = \chi^{ee}\cdot\mathbf{E}_\omega + \chi^{em}\cdot\mathbf{B}_\omega + \chi^{eQ}:\nabla\mathbf{E}_\omega$$

$$\mathbf{M}_\omega = \chi^{me}\cdot\mathbf{E}_\omega \qquad \mathbf{Q}_\omega = \chi^{Qe}\cdot\mathbf{E}_\omega$$



- **Second-order response**

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

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

Multipole symmetries

- **Second-harmonic generation**

$$P_i = \chi_{ijk}^{eee} E_j E_k + \chi_{ijk}^{eem} E_j B_k + \chi_{ijkl}^{eeQ} E_j \nabla_k E_l$$

axial **4th rank**

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

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

Isotropic material

- **Effective bulk polarization**

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

$\nabla \cdot \mathbf{E}_\omega = 0$ → $\chi^{surface}$ → separable bulk contribution

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

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

  - isotropic surface symmetry

→ **measurable components**

$$\chi_{zzz}^{s,eff} = \chi_{zzz}^{s} + \gamma$$

$$\chi_{zxx}^{s,eff} = \chi_{zxx}^{s} + \gamma$$

$$\chi_{xxz}^{s,eff} = \chi_{xxz}^{s}$$

Multipolar?

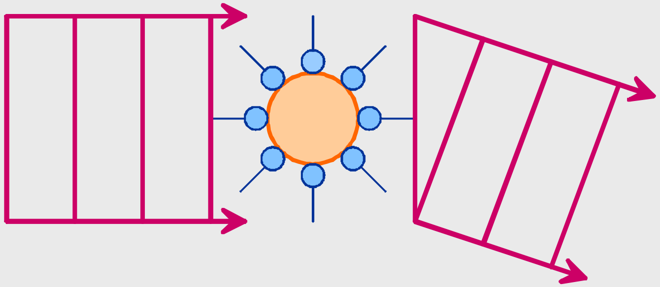
- **Light-matter interaction Hamiltonian**

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

$$\chi^{eee} \quad \chi^{eem} \quad \chi^{eeQ} \quad \chi^{mee} \quad \chi^{Qee}$$

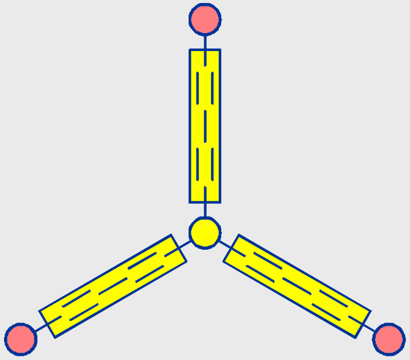
➡ **multipolar susceptibilities**

- **Scattering** (Heinz, Dadap, Brevet, …)
  - dipolar interaction
  - retardation across particles



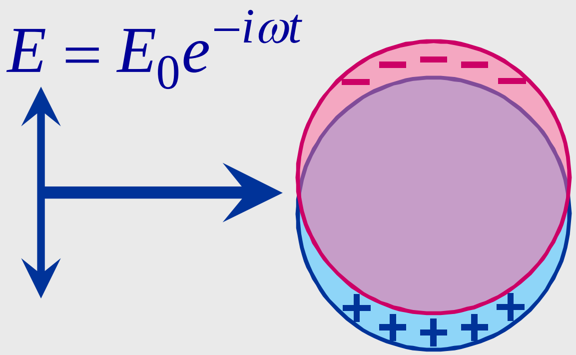
➡ **Mie-type multipolar radiation patterns**

- **Multipolar structures** (Zyss, …)
  - octupolar molecules

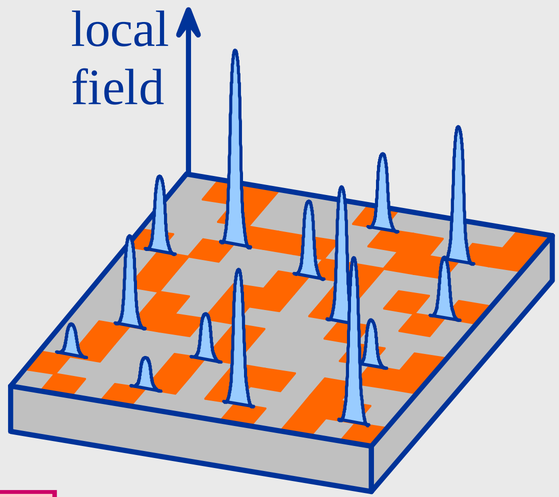


Metal nanoparticles

- **Plasmon resonances**
  - collective oscillations of conduction electrons



- **Resonances depend on**
  - size and shape
  - mutual ordering and coupling
  - dielectric environment



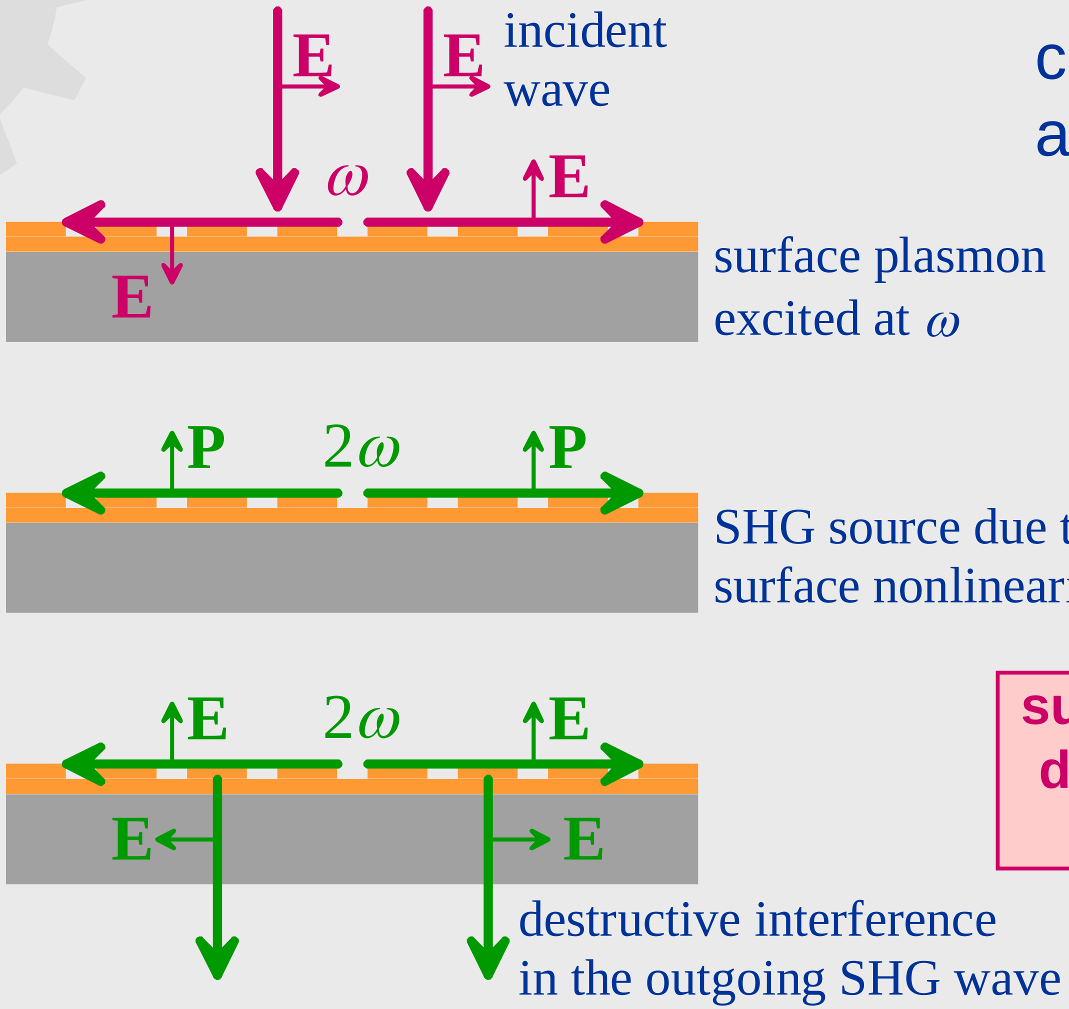
- **Nanoscale variations**
  - local fields
  - ”hot spots”

→ **enhanced nonlinear response**

  - material properties
  - strong gradients

→ **multipole effects**

Symmetry rules and plasmons

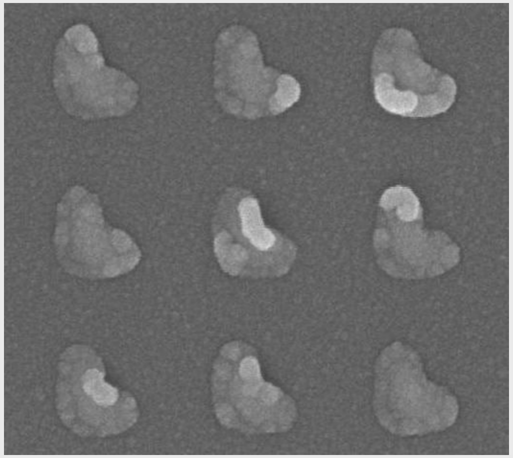


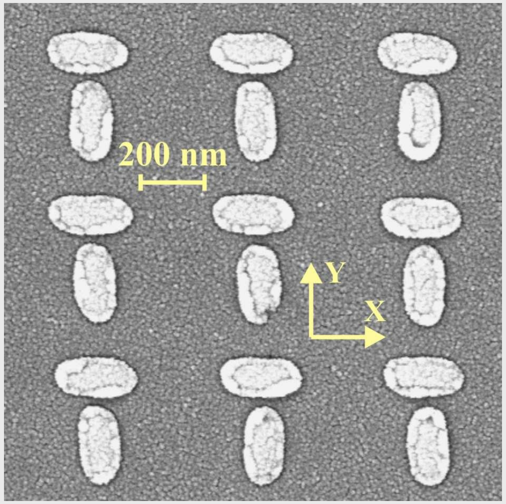
centrosymmetric system at normal incidence

surface plasmon excitation does not violate the basic symmetry rules

Second-order response

- **Symmetry rule**
  - noncentrosymmetric structures needed
- **Normal incidence**
  - avoid coupling with the traditional surface nonlinearity
  - the sample must appear noncentrosymmetric
- **Basic shapes**
  - L-shaped nanoparticles
  - T-shaped nanodimers with a nanogap



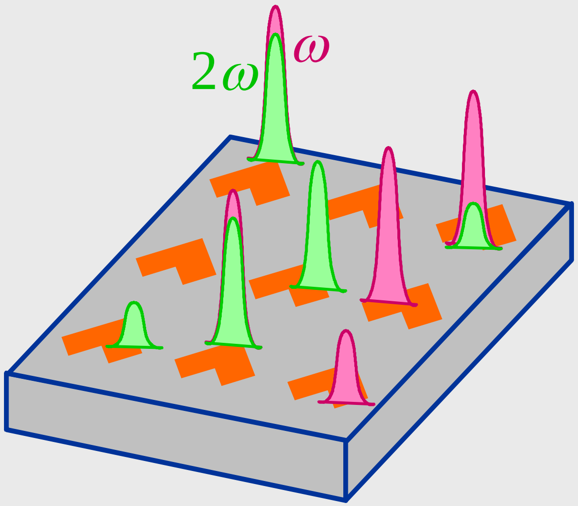


Theoretical descriptions

- **Traditional susceptibility**

$$P_i(2\omega) = \sum_{j,k} \chi_{ijk} E_j(\omega) E_k(\omega)$$

nanoscale variations



- **Effective medium approach?**
  - sub-wavelength structure
  - resonant surface modes exist

excitation depends on experimental details

- **Proper approach**
  - coupling of radiation fields to modes
  - local material properties
  - local nonlinear sources

Dadap et al.,
PRL **83**, 4045 (1999)
JOSAB **21**, 1328 (2004)

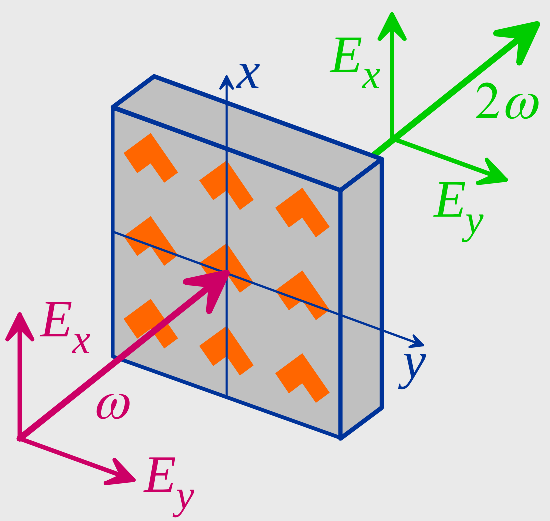
Nonlinear response tensor

- **Definition** [JOptA **8**, S278 (2006)]
  - macroscopic input-output fields (”scattering matrix”)

$$E_i(2\omega) = \sum_{j,k} A_{ijk} E_j(\omega) E_k(\omega)$$

- **Disadvantage**
  - specific to experiment, not the sample itself
- **Advantages**
  - avoids nanoscopic difficulties
  - directly measurable quantities
  - **all multipoles implicit**
  - normal incidence

→ **electric-dipole selection rules**



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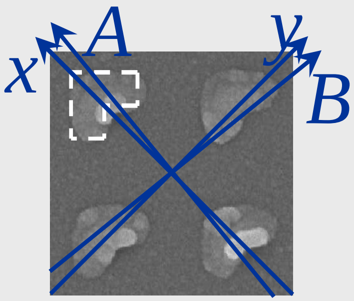
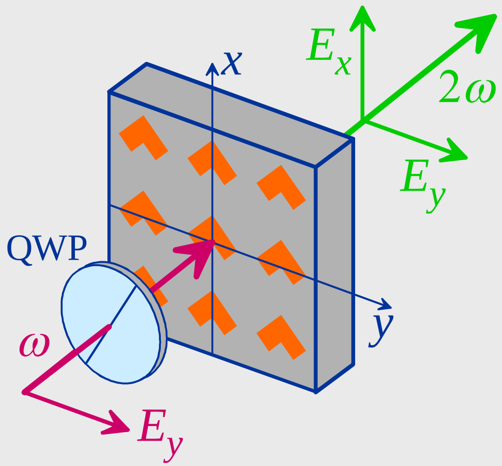
Earlier results

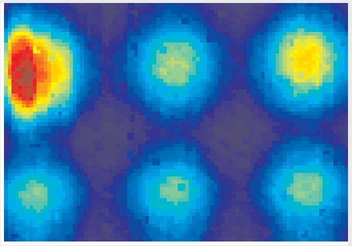
- **Linear spectra**
  [JOptA **7**, S110 (2005); APL **86**, 183109 (2005)]
  – axis shifts and dispersion of axes
  – optical activity



- **Second-harmonic response**
  [Opt. Exp. **12**, 5418 (2004); **14**, 950 (2006)]
  – ”forbidden signals”
  – circular-difference effects
  – chiral symmetry breaking due to defects



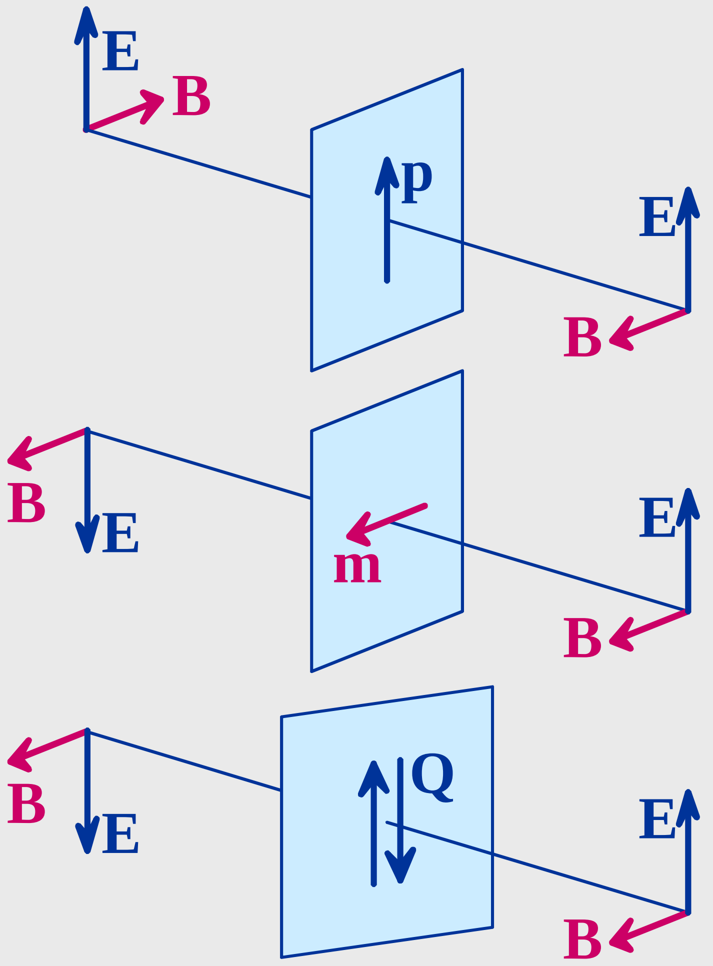
- **Nonlinear microscopy of nanodots**
  [New J. Phys. **10**,013001 (2008)]
  – inhomogeneous tensorial SHG and THG



Multipole effects

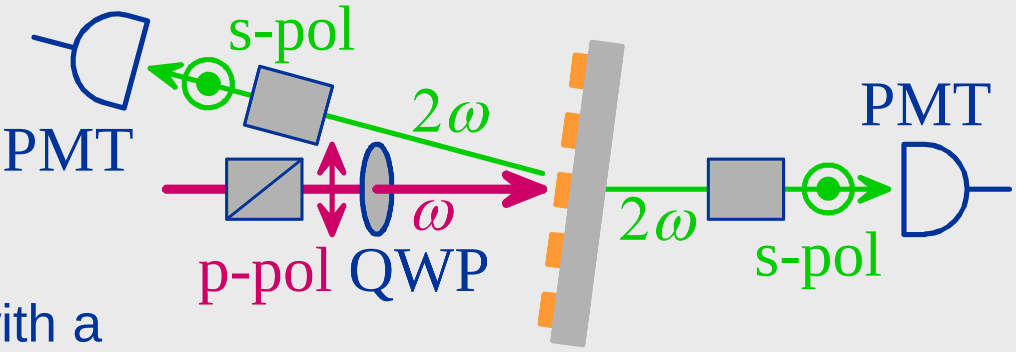
- **Multipole sources**
  - electric dipoles
  - magnetic dipoles
  - electric quadrupoles

➡ **opposite interference in transmission and reflection**



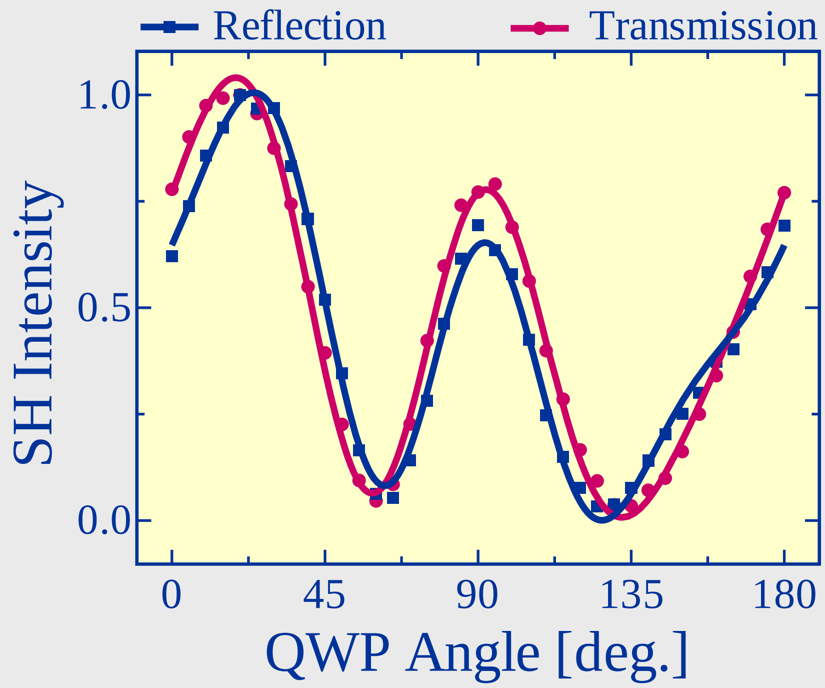
- **Higher multipoles**
  - magnetic dipoles and electric quadrupoles cannot be separated?
  - can be separated from electric dipoles

Multipole experiment



- **Fundamental beam**
  - modulate polarization with a quarter-wave plate
- **Second-harmonic signals**
  - s-polarized detection
  - compare reflected and transmitted lineshapes

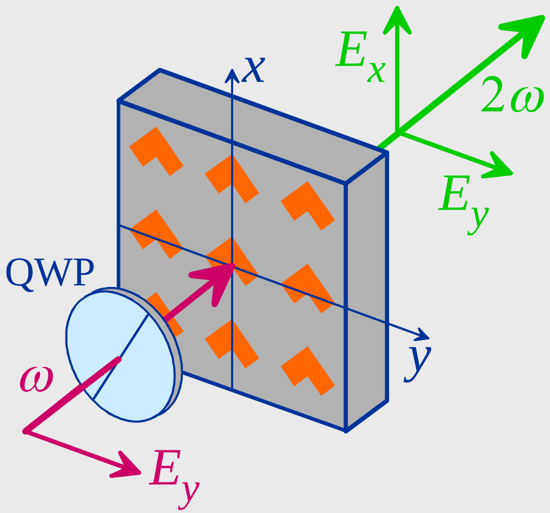
clear differences observed



Tensor analysis

- **Fundamental beam** [JOptA **8**, S278 (2006)]
  – QWP modulation of polarization
- **SHG signal**
  – detect several polarizations

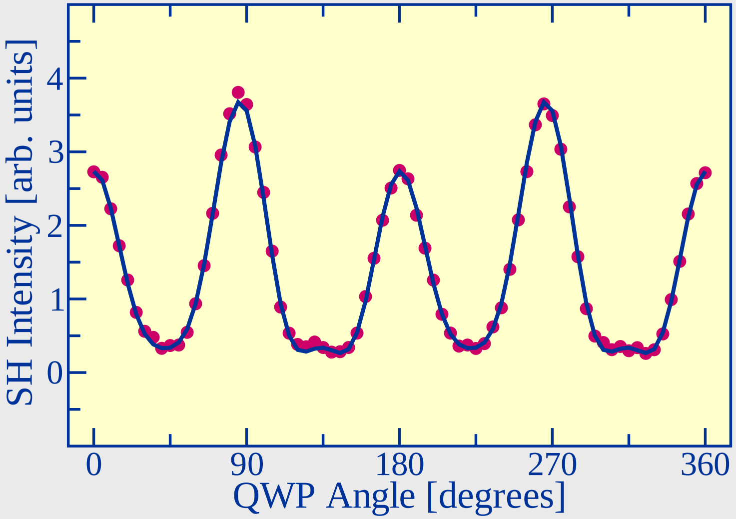
$$E_i(2\omega) = f_i E_x^2 + g_i E_y^2 + h_i E_x E_y$$



- **Fit coefficients**

$$f_{x \pm y} = A_{xxx} \pm A_{yxx}$$

→ **relative complex values of A_{ijk}**



Results of tensor analysis

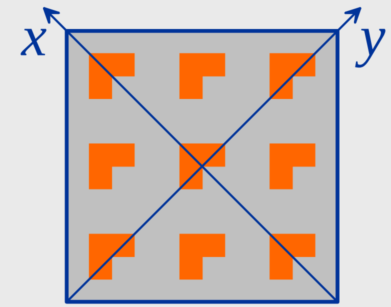
- **Symmetric and antisymmetric parts**

assume dipolar

$$A_{xxx} = A^{s}_{xxx}$$ allowed resonant

$$A_{xyy} = A^{s}_{xyy} \pm A^{as}_{xyy}$$ allowed nonresonant

$$A_{xxy} = A^{s}_{xxy} \pm A^{as}_{xxy}$$ forbidden (chiral)



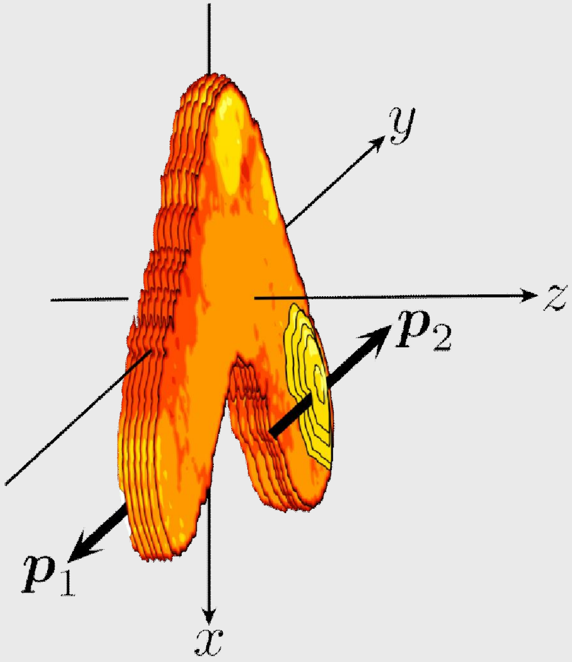
- **Result** [PRL **98**, 167403 (2007)]

	transmission	reflection	$\lvert A^{s}\rvert$	$\lvert A^{as}\rvert$
xxx	1	1	1	1
xyy	0.66 - 0.58*i*	0.37 - 0.67*i*	0.81	0.15
xxy	0.51 - 0.13*i*	0.37 - 0.26*i*	0.48	**0.10**

higher multipole amplitude ~20%

Phenomenological model

- **Full tensor analysis**
  - ”forbidden” signals dominate and have strong multipole part
  - chiral symmetry breaking
- **Role of surface defects**
  - non-equivalent defects at symmetrically opposite sites
  - local dipolar sources retarded along the direction of observation

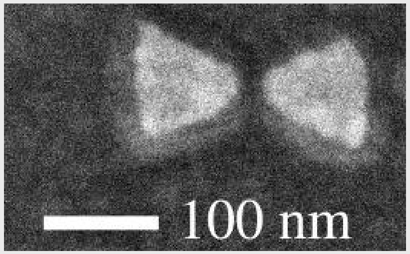


$$\mathbf{E}(2\omega) = \mathbf{p}_1 e^{-ika/2} + \mathbf{p}_2 e^{+ika/2} \approx \mathbf{p}_1 + \mathbf{p}_2 + ika(\mathbf{p}_2 - \mathbf{p}_1)/2$$

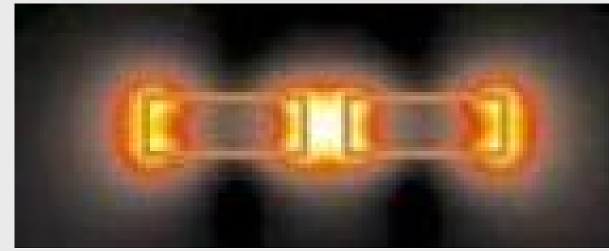
effective dipole

effective quadrupole

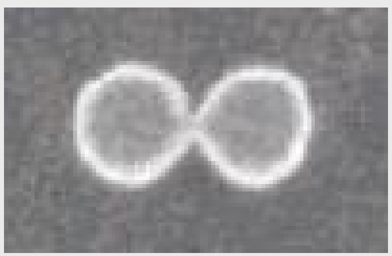
Enhancement in nanogaps



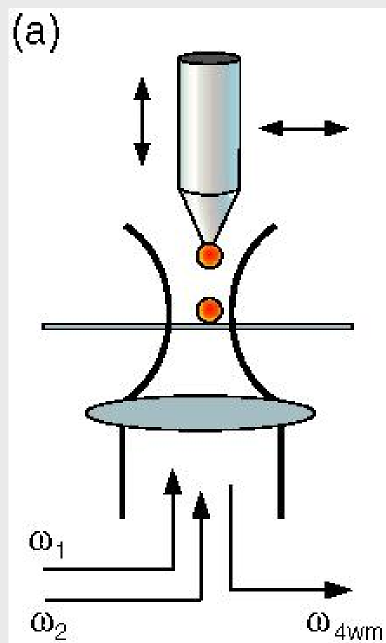
bowtie antenna
[Fromm et al.,Nano Lett. **4**, 957 (2004)]



resonant antenna
[Mühlschlegel et al., Science **308**, 1607 (2005)]



coupled dimers
[Atay et al., Nano Lett. **4**, 1627 (2004)]

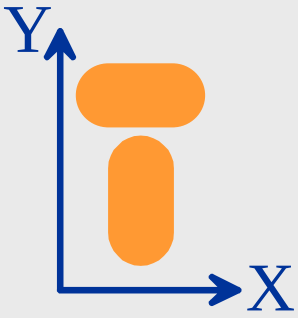


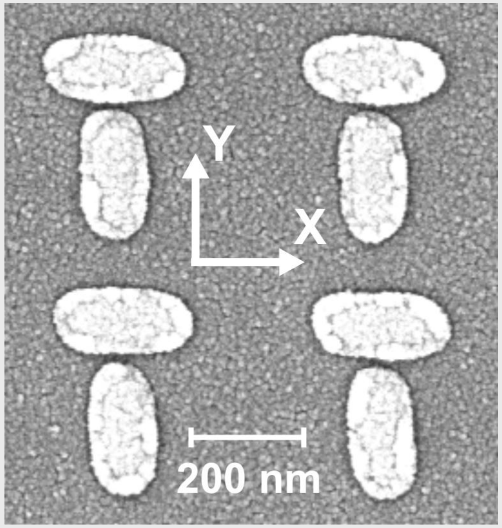
gap-dependent FWM
[Danckwerts and Novotny, PRL **98**, 026104 (2007)]

self-similar spheres for SHG
[Li et al., PRB **72**, 153401 (2005)]

Designer dimers for SHG

- **Symmetry rule**
  - noncentrosymmetric structures needed
- **Nanodimers** [Nano Lett. **7**, 1251 (2007)]
  - T shape
  - noncentrosymmetric
  - vary gap between the bars
  - resonant with 1060 nm laser
- **Expected result**
  - only Y polarization enhanced
  - smallest gap leads to largest enhancement

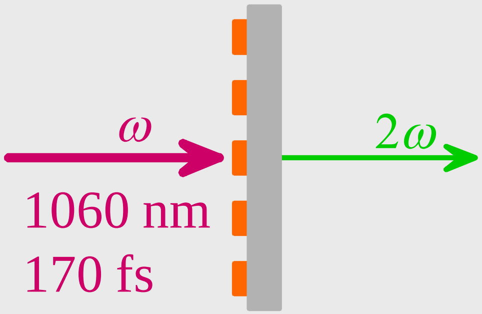


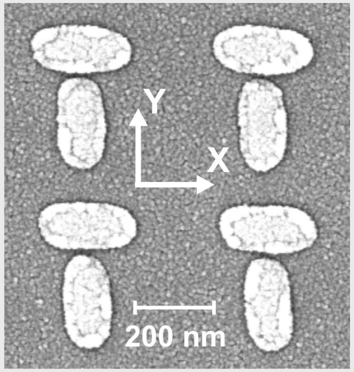


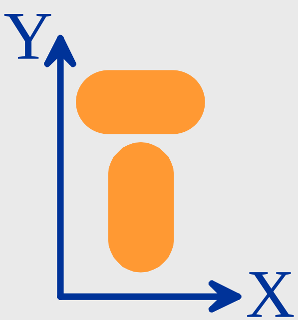
Gap dependence of SHG

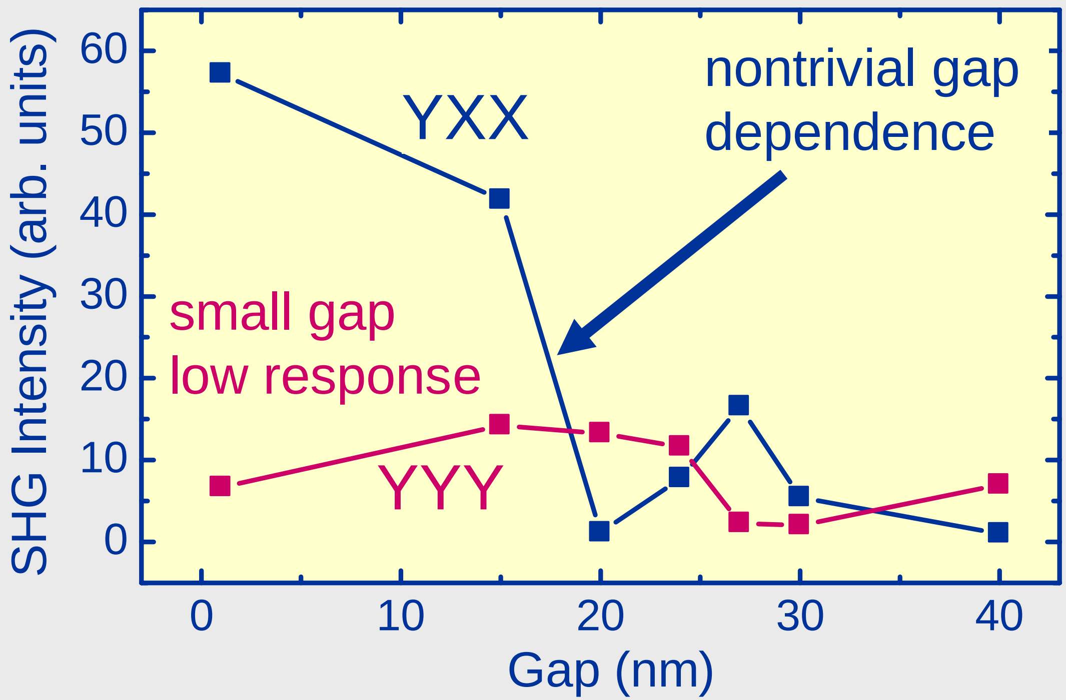
- **SHG signals allowed by symmetry**
  - pure polarization combinations for normal incidence

$$A_{YXX}\,,\ A_{YYY}$$







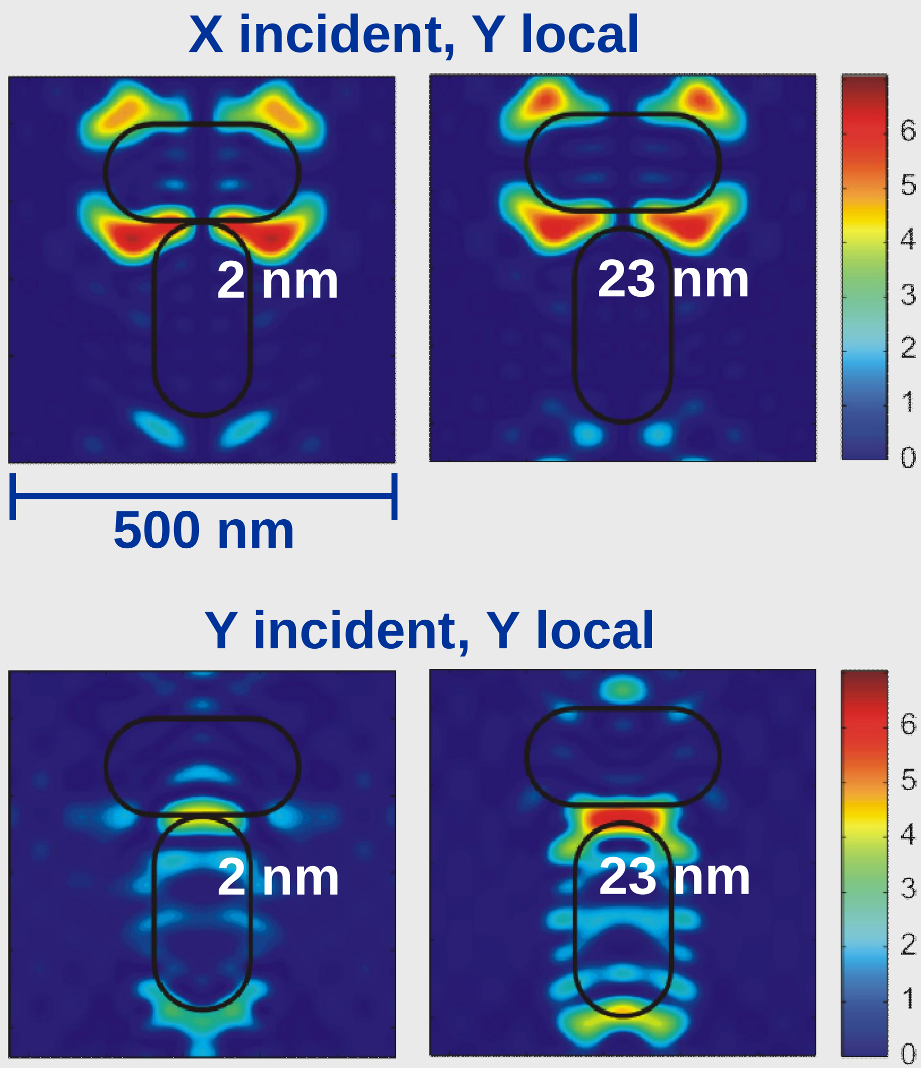


Calculated local-field distributions

- **Fundamental field**
  - plasmon resonance with the dimer
  - strong local-field effects
  - polarization conversion

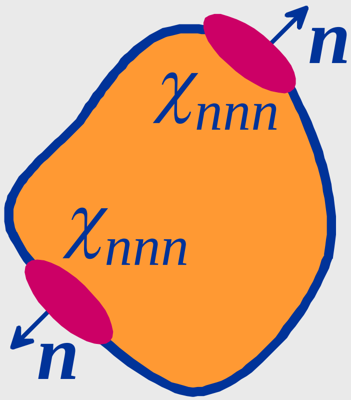
local field contains new polarization components

- **Second-harmonic field**
  - off-resonant
  - weak local-field effects



Origin of SHG

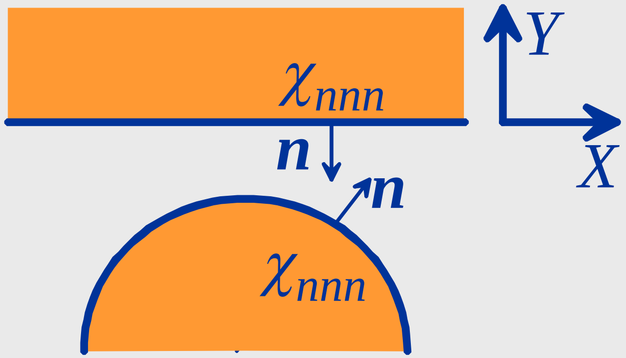
- **Local-field distribution**
  - hot spots near the boundary of the dimer



- **Surface nonlinearity**
  - dominated by local component χ_{nnn}
  - integrate response around dimer perimeter

→ **parts with opposite normal tend to cancel** → **asymmetric field distribution required**

- **Gap region**
  - formally noncentrosymmetric
  - responses from top and bottom tend to cancel

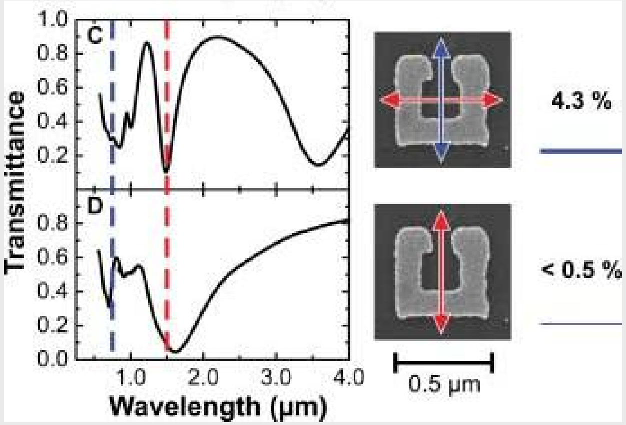


[Nano Lett. **7**, 1251 (2007)]

Metal nanoparticles

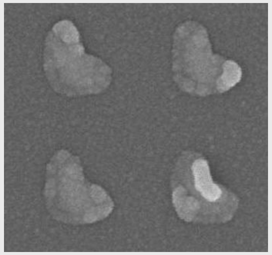
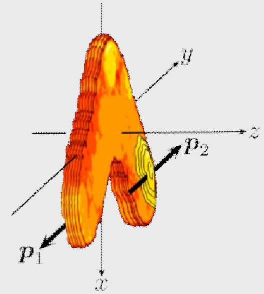
- **Metamaterials** [Wegener et al., Science **313**, 502 (2006); Opt. Lett. **33**, 1975 (2008)]
  - Lorentz force $\mathbf{F} \sim \mathbf{v} \times \mathbf{B}$
  - convective forces $\mathbf{F} = (\mathbf{v} \bullet \nabla)\mathbf{v}$

  → **bulk nonlinearity**

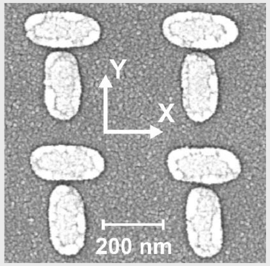


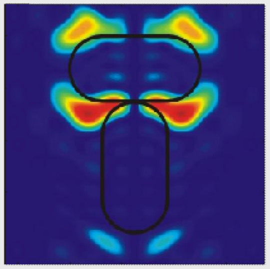
- **Our interpretation**
  - T samples
  - role of surface defects

  → **surface nonlinearity**

- **Free-electron theories**
  - bulk parameter vanishes → $\delta' = 0$





Surface and bulk contributions

z

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

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

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

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

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

Isotropic material

- **Effective bulk polarization**

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

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

$\chi^{surface}$

separable bulk contribution

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

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

  - isotropic surface symmetry

→ **measurable components**

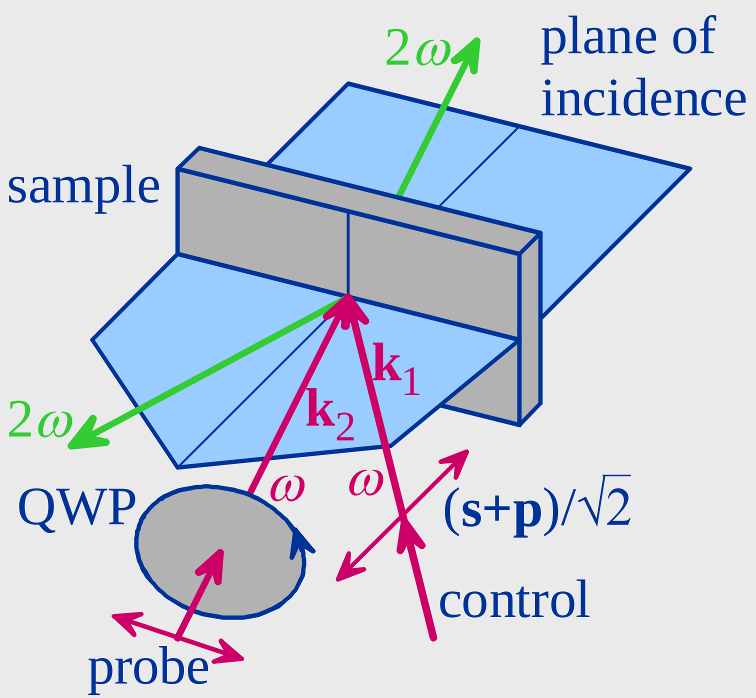
$$\chi_{zzz}^{s,eff} = \chi_{zzz}^{s} + \gamma$$

$$\chi_{zxx}^{s,eff} = \chi_{zxx}^{s} + \gamma$$

$$\chi_{xxz}^{s,eff} = \chi_{xxz}^{s}$$

Experiment: Two-beam SHG

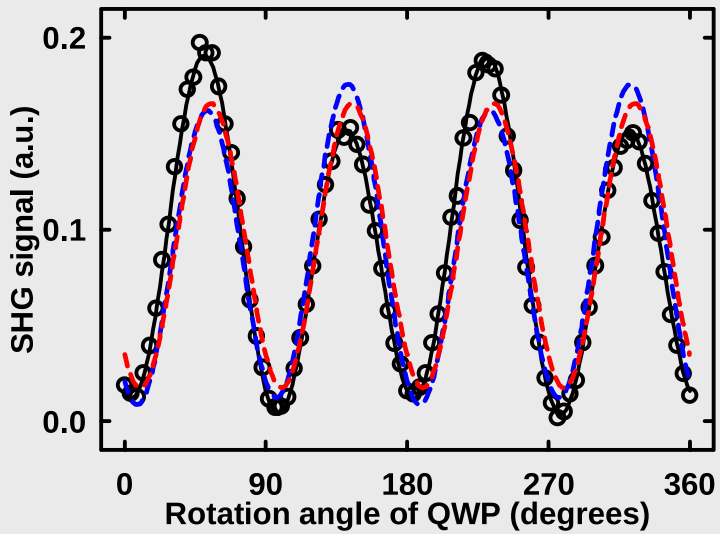
- **Fundamental beams**
  - 70 ps, 1064 nm, 1 kHz Nd:YAG
- **Control beam**
  - polarization fixed
- **Probe beam**
  - polarization varied by QWP
- **SHG signal**
  - reflected
- **Sample**
  - 150 nm thick gold film
  - glass substrate
  - linear properties determined by ellipsometry



Results

- **s-polarized SHG signal**
  - can only be fitted by surface-bulk interference

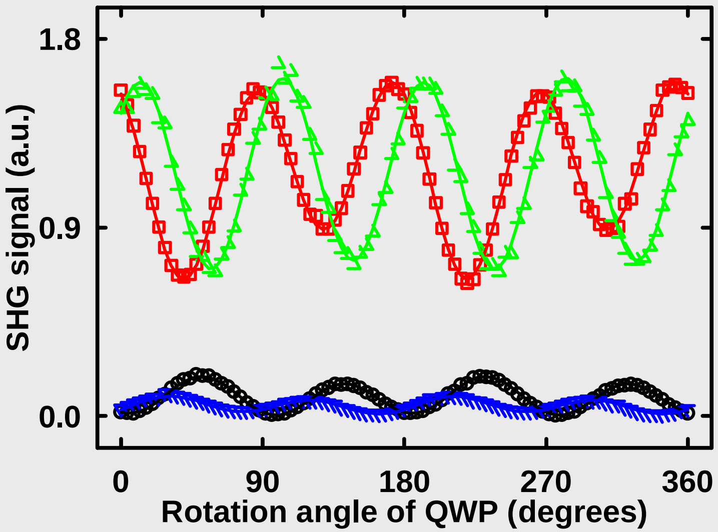
→ $\delta' \neq 0$



- **Theoretical explanation**
  - add momentum damping to the hydrodynamic model

- **Polarization measurements**
  - different combinations of control and SHG polarizations
  - simultaneous fit of all data

→ **tensor components**



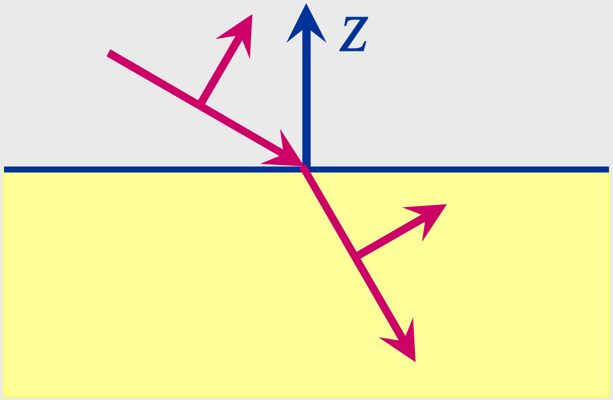
Results for gold film

- **Nonlinear tensor components** [PRB **80**, 233402 (2009)]

	component	relative magnitude	relative contribution to dominant signal
surface	$\chi_{zzz}+\gamma$	250	1.3
surface	$\chi_{zxx}+\gamma$	1	1.5
surface	χ_{xxz}	3.6	**3.5**
bulk	δ'	2.7	0.004

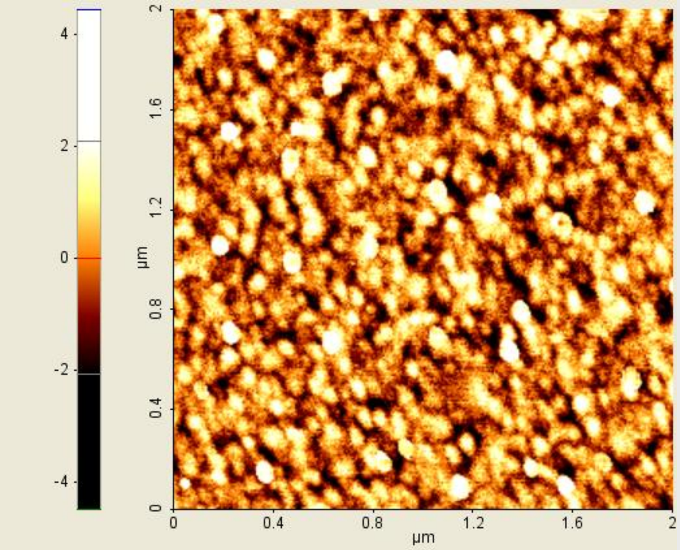
based on internal fields

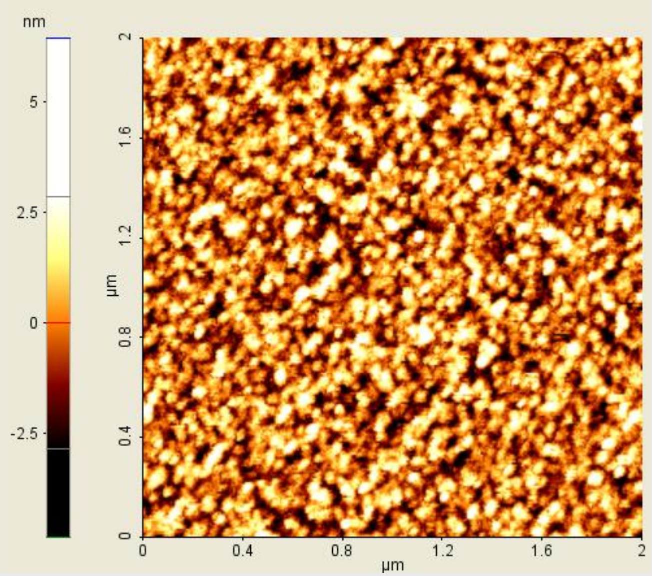
Surface effects should not be neglected!!!

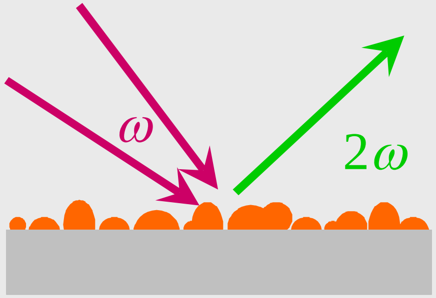


Thick and thin films

- **Thick film**
  - 150 nm nominal thickness
  - isolated terraces removed
  - rms roughness 1.1 nm
  - peak-to-peak roughness 8.9 nm
- **Thin film**
  - 20 nm nominal thickness
  - rms roughness 1.5 nm
  - peak-to-peak roughness 11.3 nm



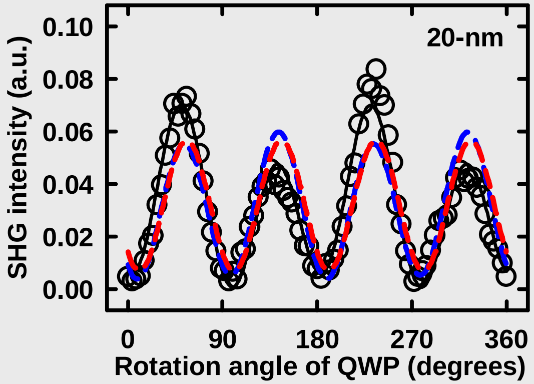




SHG measurements

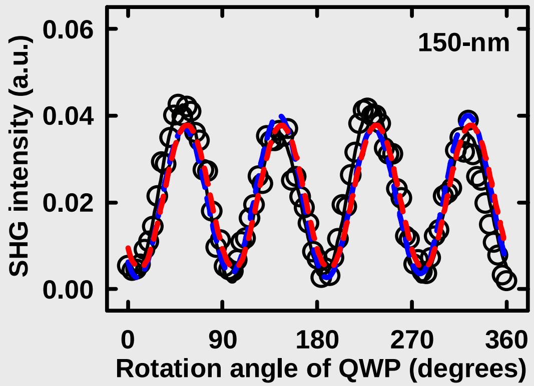
- **s-polarized signals**

$$A_{2\omega} = F^{surface}\left(A_{1p}A_{2s} + \frac{\sin\theta_2}{\sin\theta_1}A_{1s}A_{2p}\right) + F^{bulk}\left(A_{1p}A_{2s} - A_{1s}A_{2p}\right)$$



- **Surface-bulk interference**

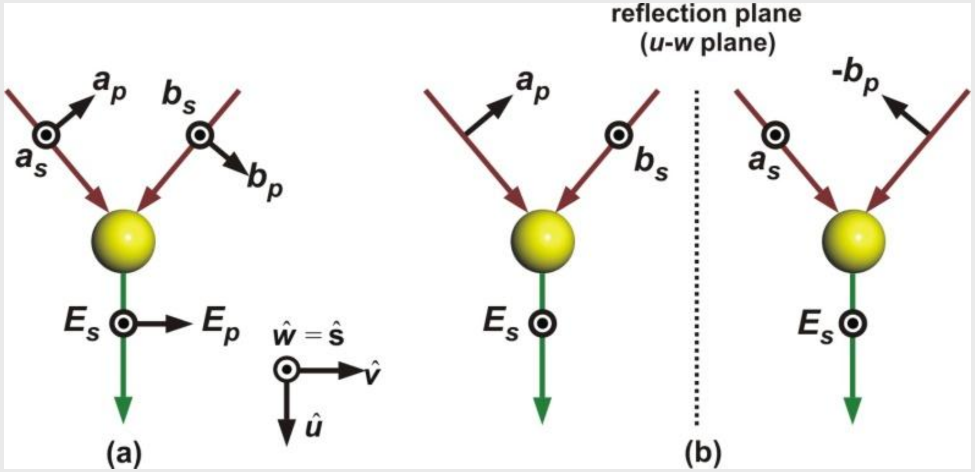
sample	$F^{surface}$	F^{bulk}
20 nm	0.2118	0.033exp(-*i*62º)
150 nm	0.1770	0.015exp(-*i*62º)



bulk-type response enhanced more by surface roughness

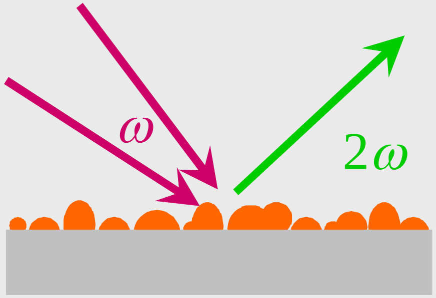
Phenomenology

- **Nanoscale feature**
  - idealized to a sphere



- **SHG geometry**
  - two fundamental beams
  - coherent signal

- **Symmetry arguments**
  - different polarizations of the fundamental beams
  - only s-polarized second-harmonic signals allowed
  - behaves as the bulk-type response



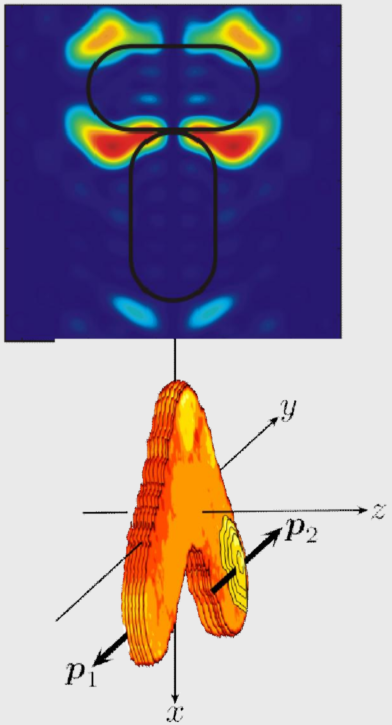
Parts of nonlinear response

- **Resonance enhancement**
  - plasmon resonance → **strong local fields**
- **Overall polarized local-field distribution**
  - plasmon resonance and structural geometry

→ **interaction with locally varying nonlinearity**

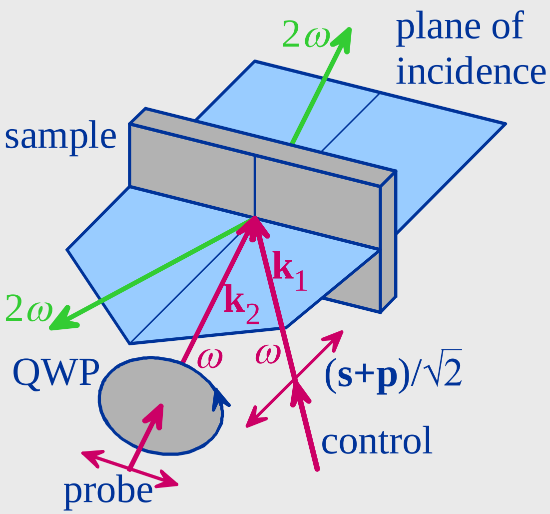
- **Small-scale features**
  - symmetry breaking
  - attract strong local fields → **local nonlinear sources**
- **Multipole effects**
  - directional properties
  - surface and bulk

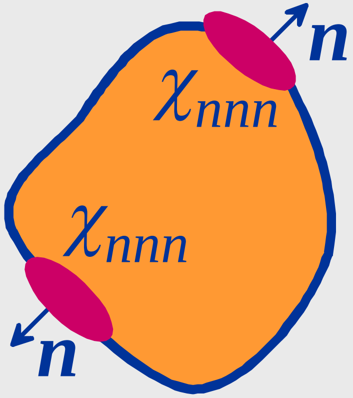
↓ **effective multipoles**



Conclusions

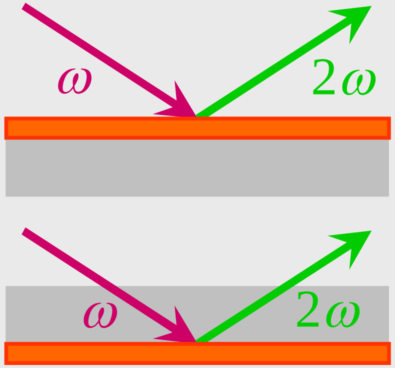
- **SHG in centrosymmetric materials**
  - dipolar surface response
  - multipolar bulk response
- **Two-beam SHG**
  - unambiguous and quantitative separation of surface and bulk effects
- **Gold**
  - first direct observation of bulk response
  - surface effects dominate
- **Implication for metamaterials**
  - nonlinear properties better described by surface than by bulk effects



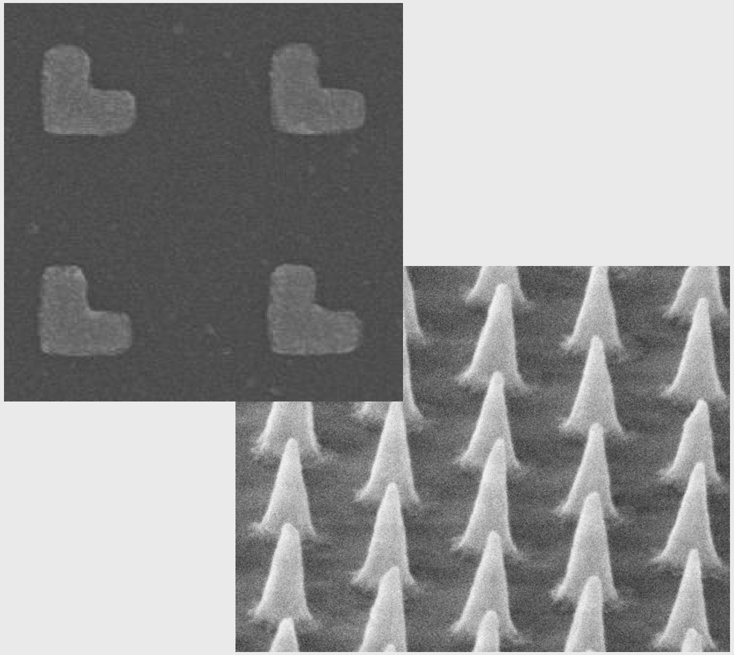


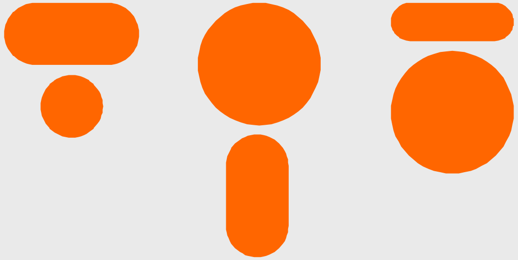
Next steps

- **Change surface properties**
  - surface response modified
  - bulk response unmodified
  - **how to separate the surface and bulk responses in the presence of roughness?**



- **Optimized nanoparticles**
  - dimers with coupled resonances
  - samples with improved quality
  - plasmons and lightning-rod effect
  - full multipole analysis





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