Nonlinear optics with metals

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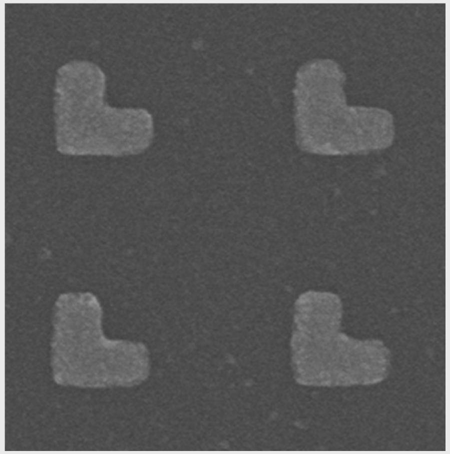
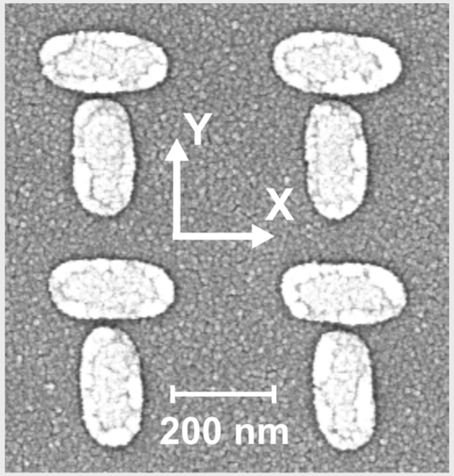
Outline

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

Second-order response

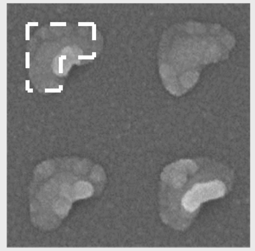
- **Symmetry rule**
  - noncentrosymmetric structures needed
- **Normal incidence**
  - avoid coupling with traditional surface nonlinearity
  - sample must appear noncentrosymmetric
- **Basic shapes**
  - L-shaped nanoparticles
  - T-shaped nanodimers with a nanogap
- **Typical sample dimensions**
  - period 400-500 nm
  - gold thickness 20 nm

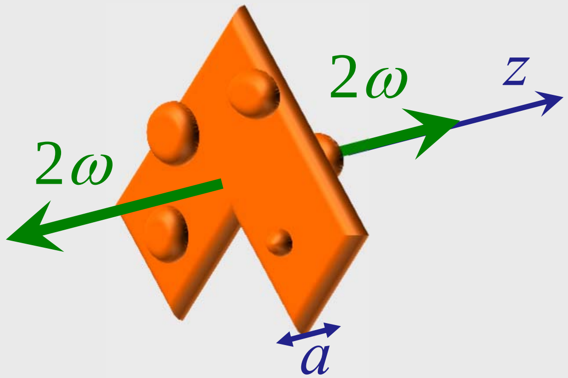




Phenomenological model

- **Full tensor analysis**
  [Opt. Express **16**, 17196 (2008)]
  - ”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





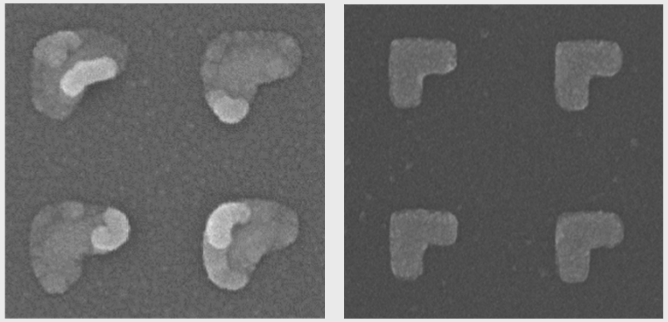
$$\boxed{\mathbf{E}(2\omega) = \mathbf{p}_1 e^{-ika/2} + \mathbf{p}_2 e^{+ika/2} \approx \mathbf{p}_1 + \mathbf{p}_2 + ika(\mathbf{p}_2 - \mathbf{p}_1)/2}$$

effective dipole

effective quadrupole

New samples

- **Significantly improved quality**
  [Opt. Express **18**, 16601(2010)]
  - narrow extinction peaks
  - high-order resonances observed
  - stronger SHG signals

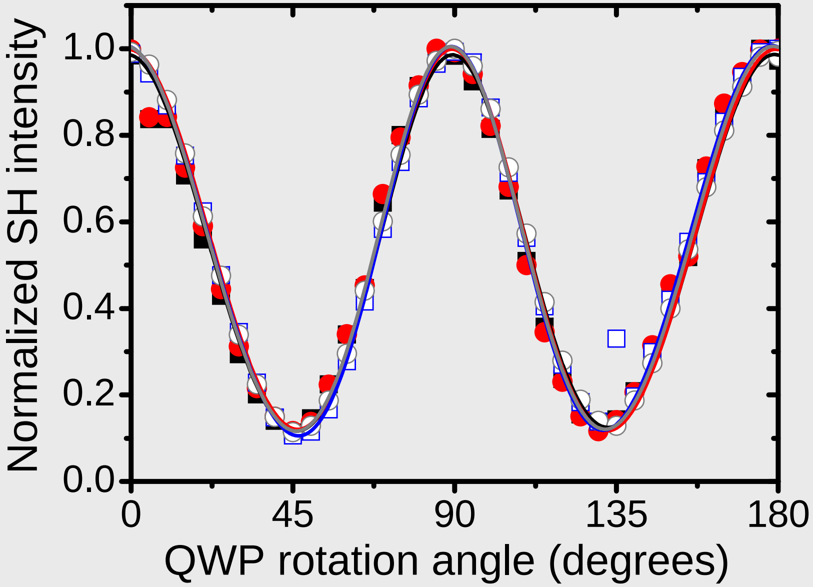


- **Four equivalent signals**
  - all lineshapes overlap

→ **effective dipole limit reached**

↓

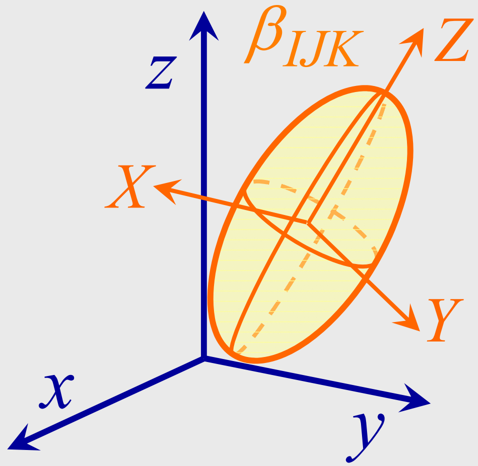
path open for tailorable nonlinear metamaterials



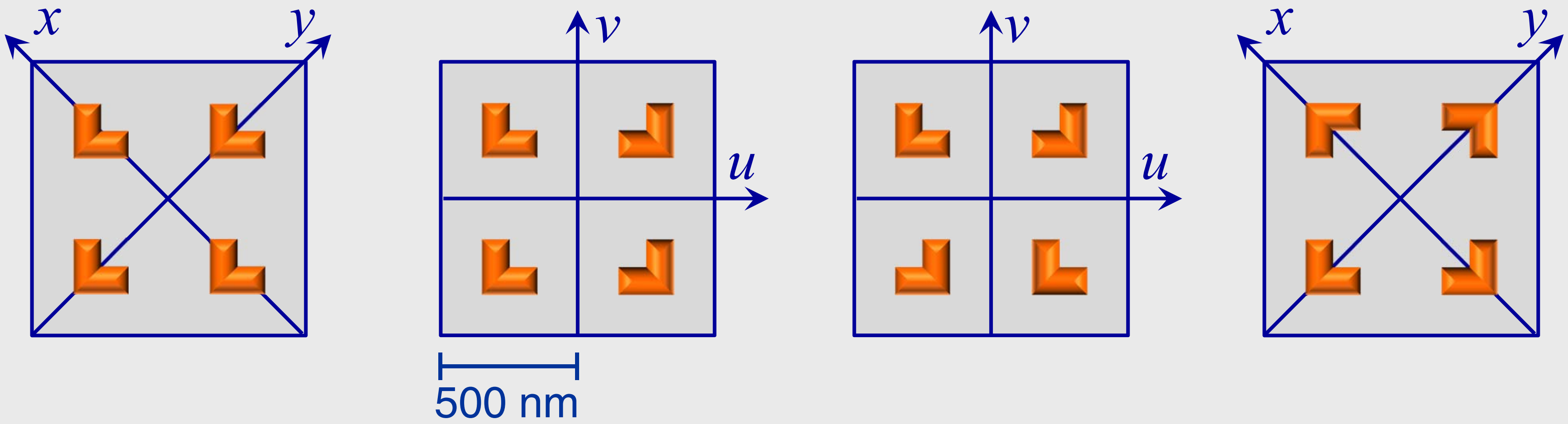
Metamolecular nonlinear optics

- **Molecular nonlinear optics**

$$\chi_{ijk} = \sum_{\text{molecules}} \beta_{IJK} \cos(i,I)\cos(j,J)\cos(k,K)$$

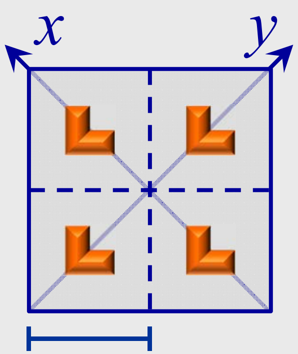


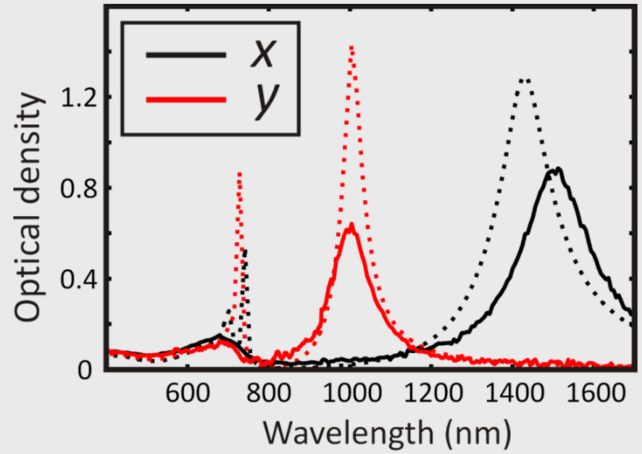
- **Metamolecule**
  - L shape
  - effective dipolar SHG response



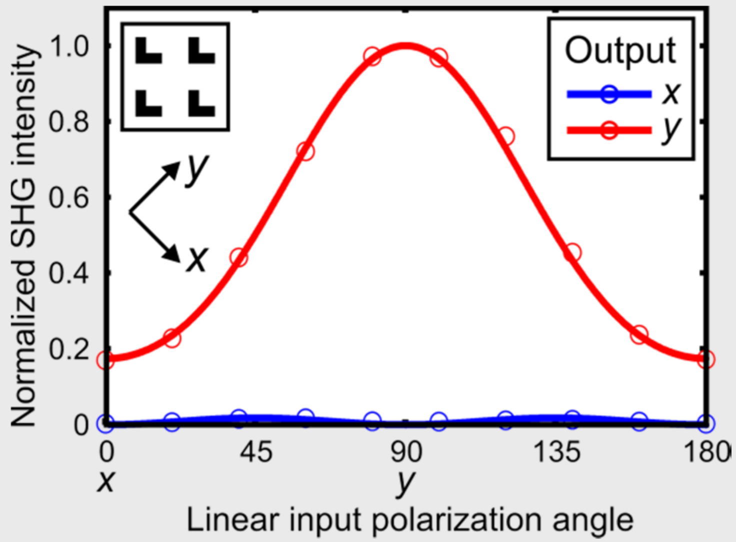
Reference sample

- **Plasmon resonances**
  - x-polarized at 1500 nm
  - y-polarized at 1000 nm



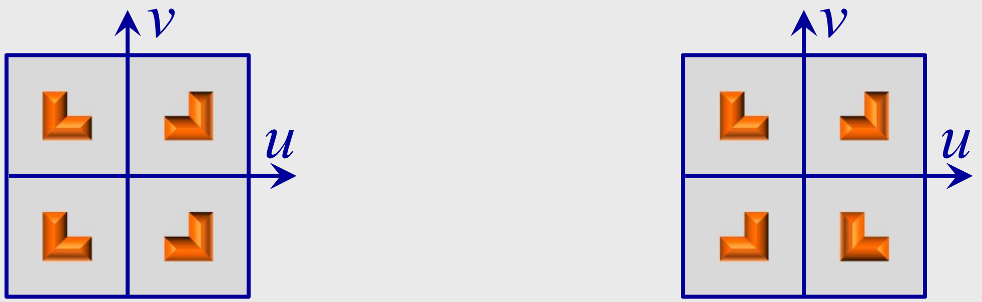


- **SHG measurement**
  - rotate linear fundamental polarization
  - detect polarization components of SHG field
  - symmetry rules fulfilled
  - strong enhancement for y-polarized resonance of fundamental light

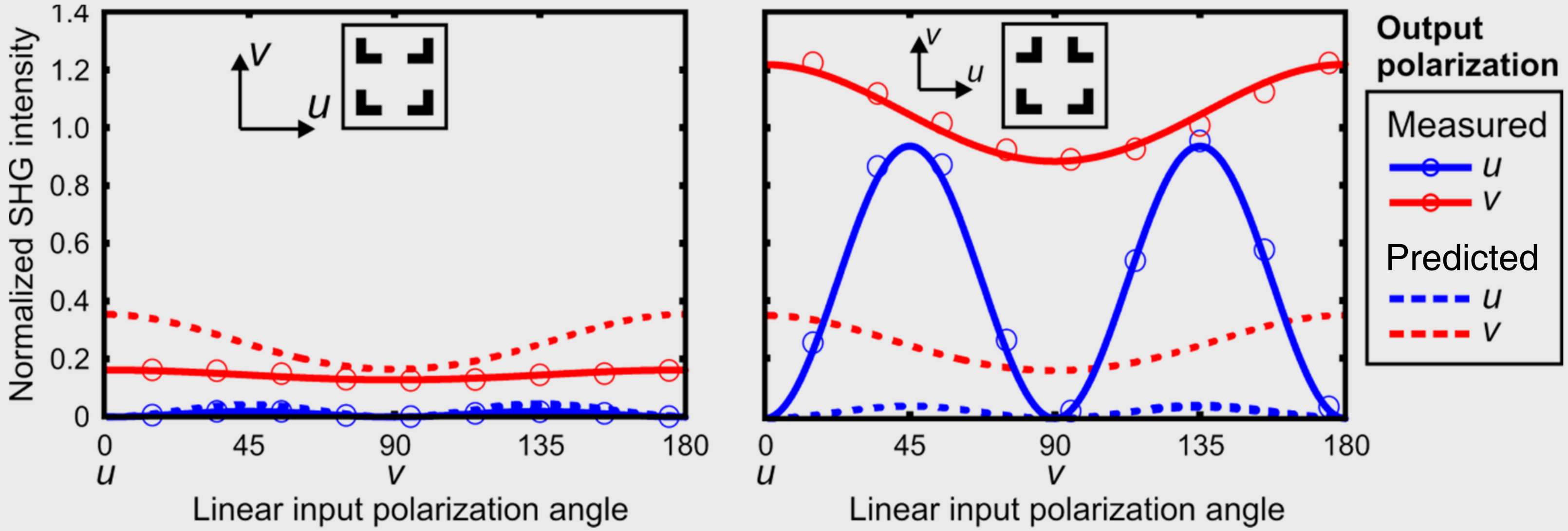


SHG from modified samples

- **Orientational average over particles**
  - prediction for modified samples

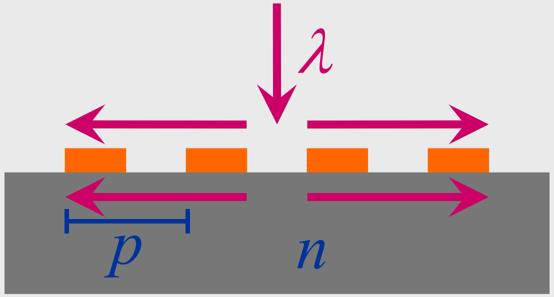


Nano Lett. **12**, 673 (2012)

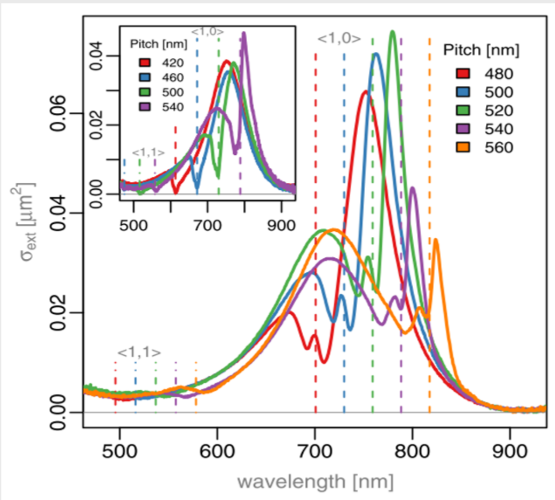


Diffractive coupling

- **Air modes** $\boxed{\lambda \le p}$
- **Substrate modes** $\boxed{\lambda \le np}$
  - need not propagate in air

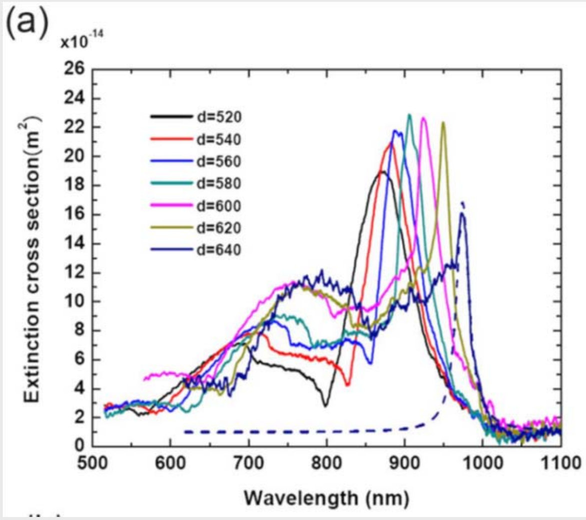


- **Plasmonic structures**
  - interplay between particle plasmons and diffraction → **sharp spectral features**



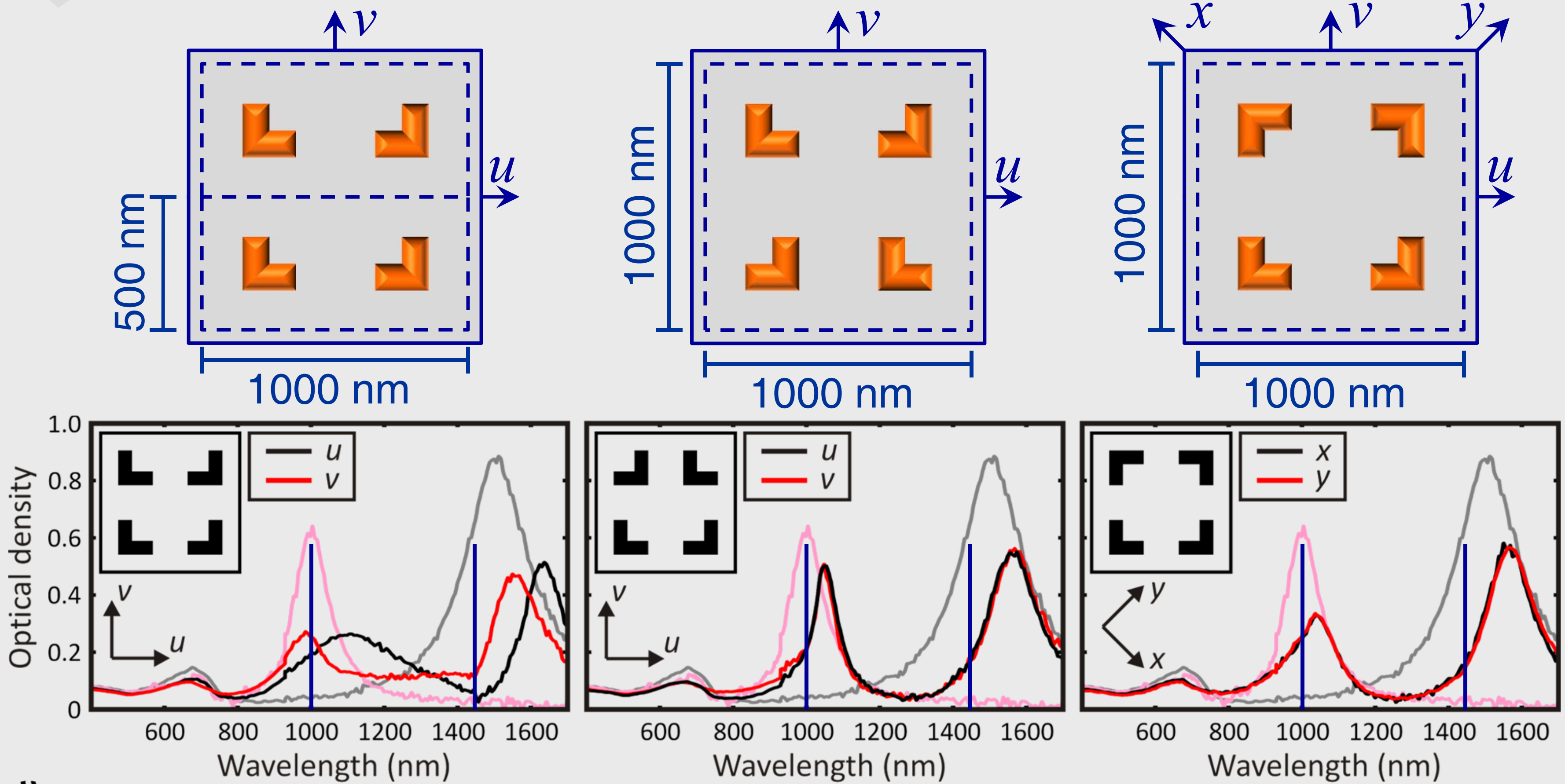
Auguié et al., PRL **101**, 143902 (2008)

Chu et al., APL **93**, 181108 (2008)



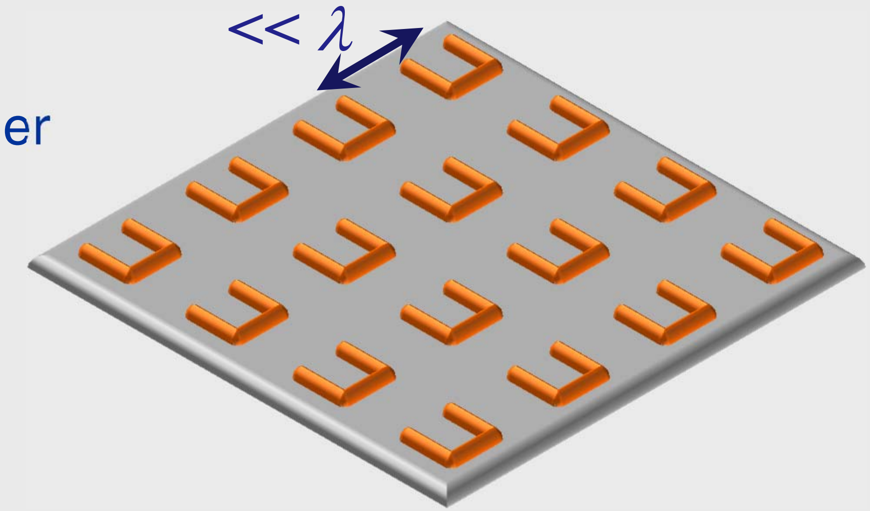
Spectra of modified samples

- **Unit cell depends on ordering** [Opt. Lett. **36**, 2375 (2011)]
  - interplay between particle plasmons and diffraction

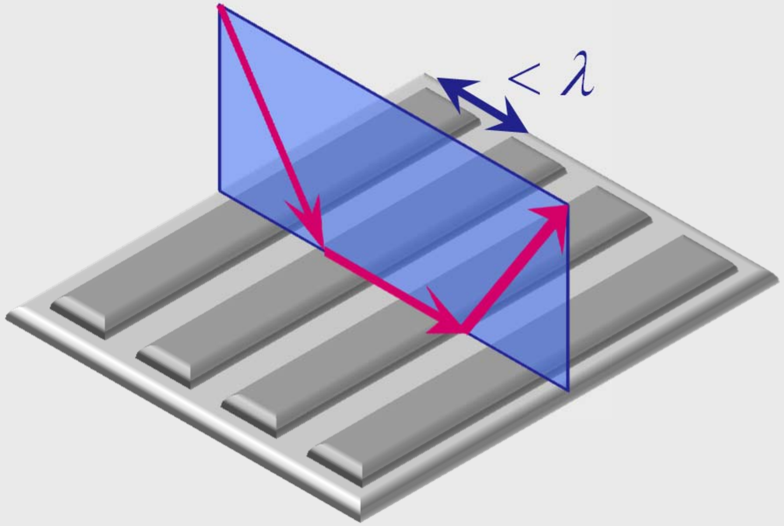


"Metamaterials"

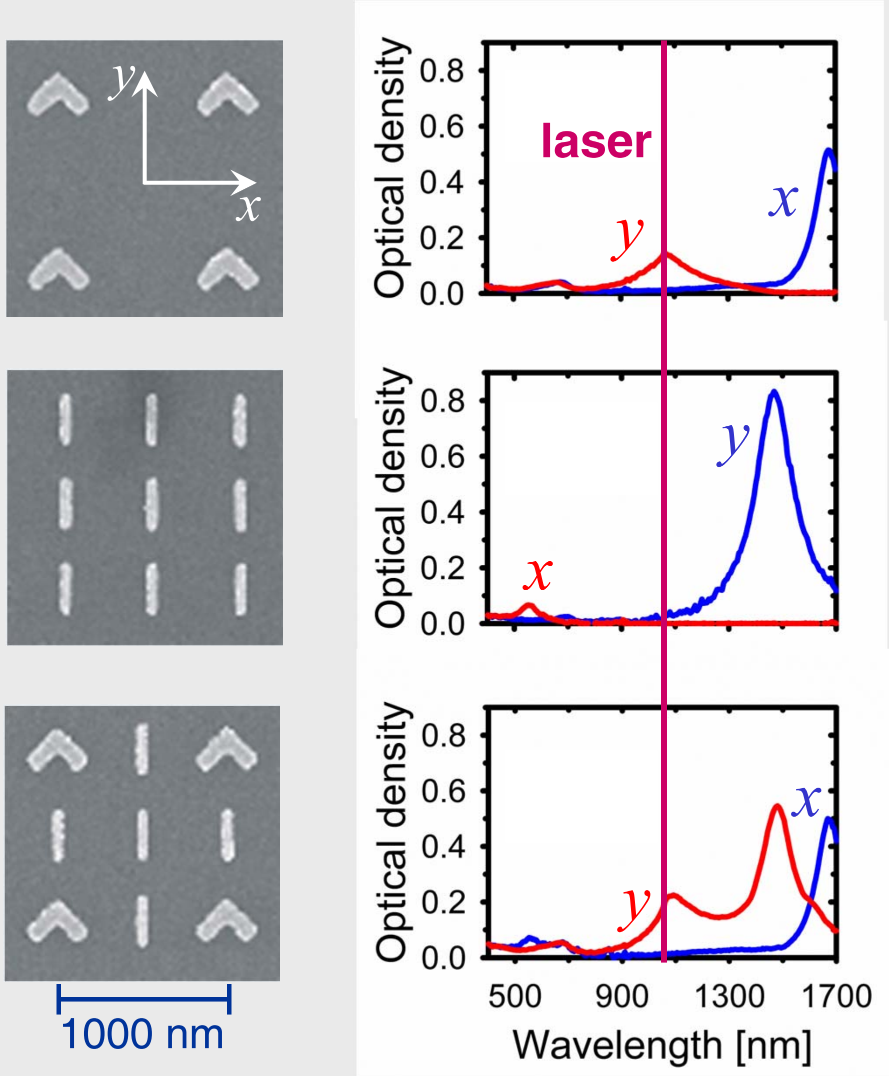
- **Effective medium**
  - structural features much smaller than wavelength
  - transformation optics
  - negative index of refraction
  - electromagnetic cloaking



- **Functional nanostructures**
  - optimized for the desired function
  - electromagnetic surface modes
  - diffraction anomalies
  - resonance-domain effects
  - also purely dielectric structures



Passive elements



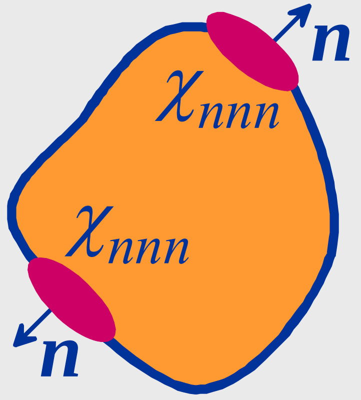
SHG signals

$$I_{yyy} = 889$$

$$I_{yyy} = 1886$$

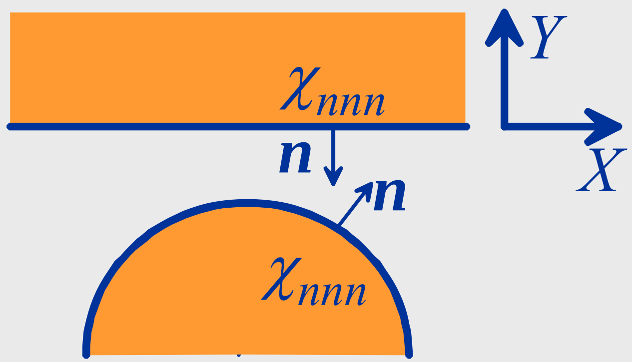
Origin of SHG

- **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

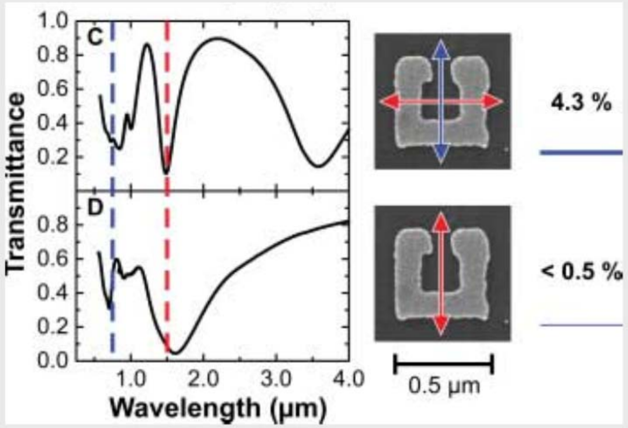


[Nano Lett. **7**, 1251 (2007)]

SHG from metal nanoparticles

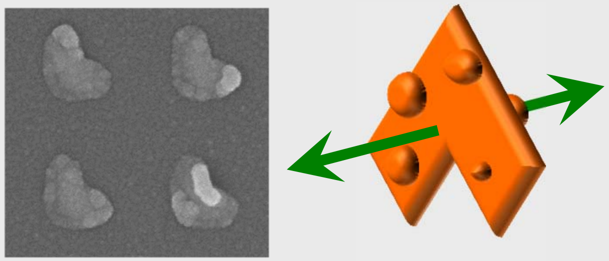
- **Metamaterials** [Wegener et al., Science **313**, 502 (2006); Opt. Lett. **33**, 1975 (2008)]
  - Lorentz force $\boxed{\mathbf{F} \sim \mathbf{v} \times \mathbf{B}}$
  - convective force $\boxed{\mathbf{F} = (\mathbf{v} \bullet \nabla)\mathbf{v}}$

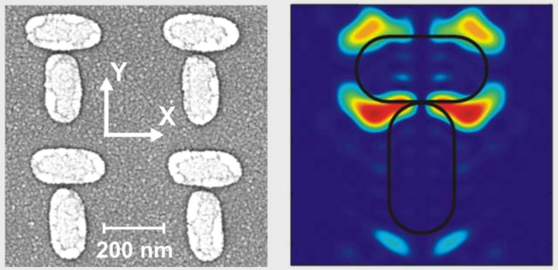
  ➡ **bulk nonlinearity**



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

  ➡ **surface nonlinearity**





- **Free-electron theories**
  - bulk parameter vanishes ➡ $\boxed{\delta' = 0}$

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Surface and bulk contributions

z

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

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

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

- **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**

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

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

$$\chi^{surface}$$

separable bulk contribution

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

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

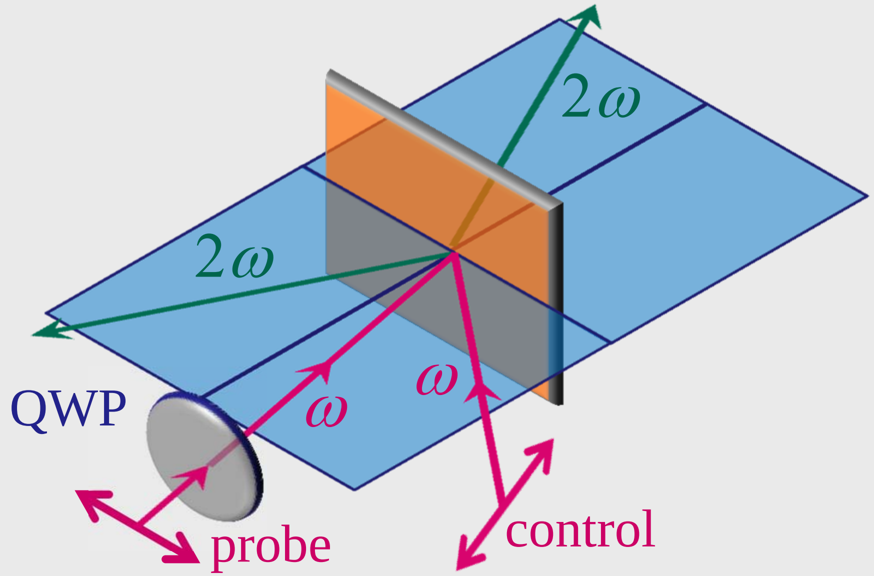
  - isotropic surface symmetry

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

measurable components

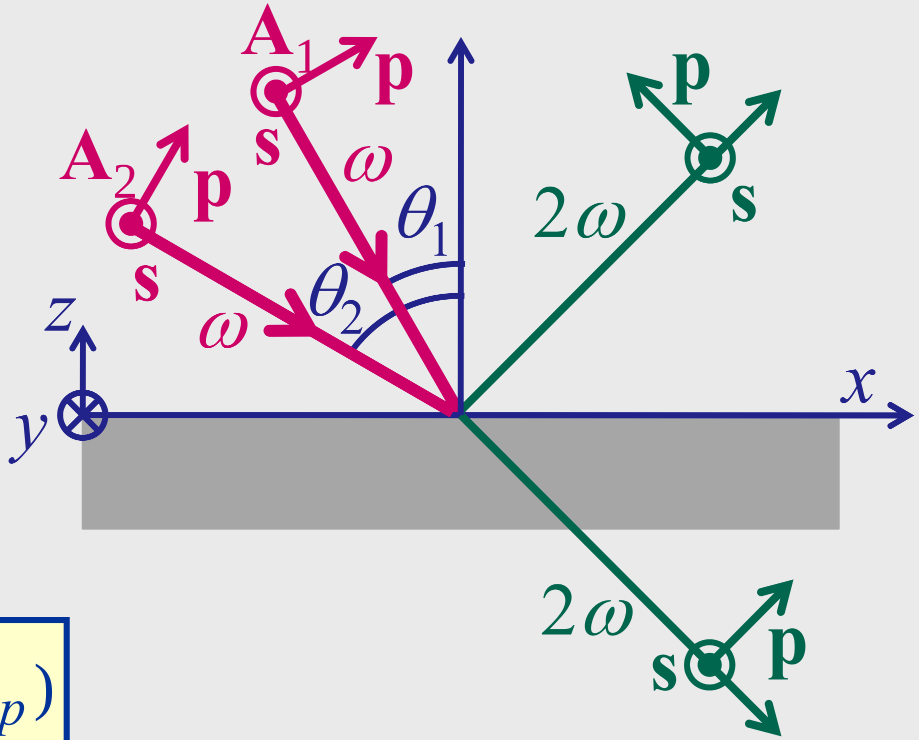
Experiment: Two-beam SHG

- **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



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**

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

PRB **72**, 033412 (2005)

Results

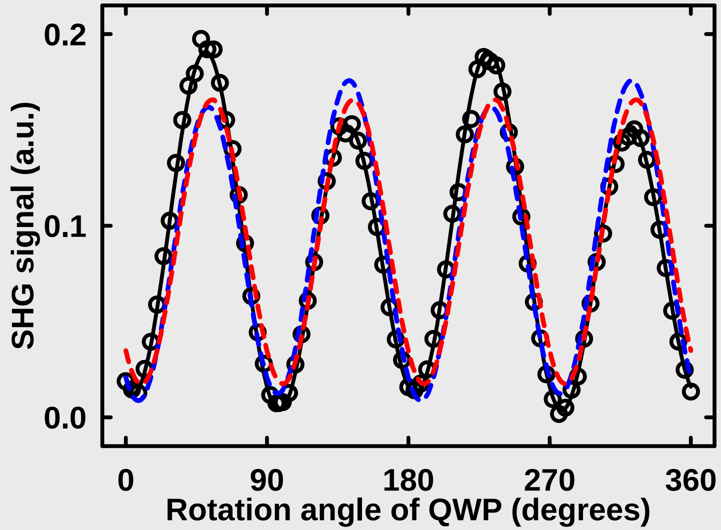
- **s-polarized SHG signal**
  - can only be fitted by surface-bulk interference

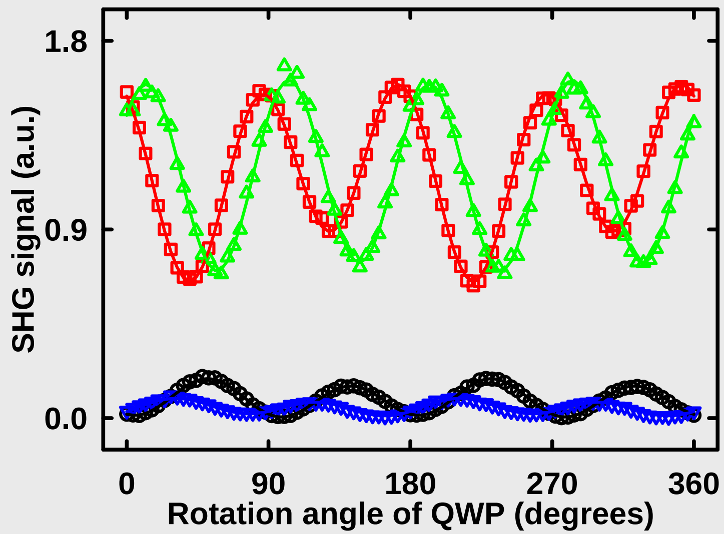
$\rightarrow$ $\boxed{\delta' \neq 0}$

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

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

$\rightarrow$ **tensor components**





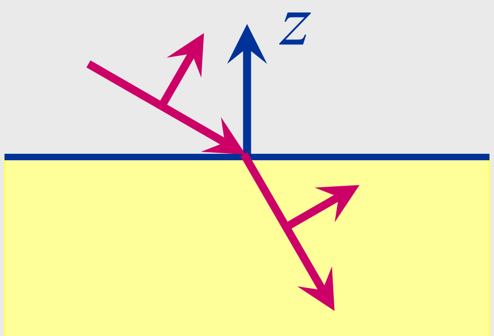
Results for gold film

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

	nonlinear parameter	relative magnitude	relative contribution to dominant signal	relative contribution to another signal
surface	$\chi_{zzz}+\gamma$	250	1.3	-
surface	$(\chi_{zxx})+\gamma$	1	1.5	-
surface	χ_{xxz}	3.6	**3.5**	2.2
bulk	δ'	2.7	0.004	**0.2**

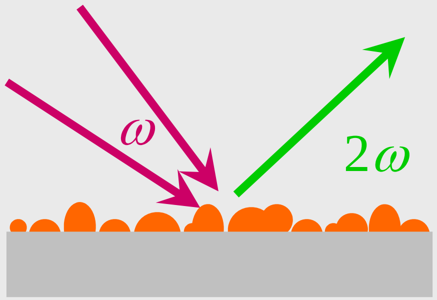
based on internal fields

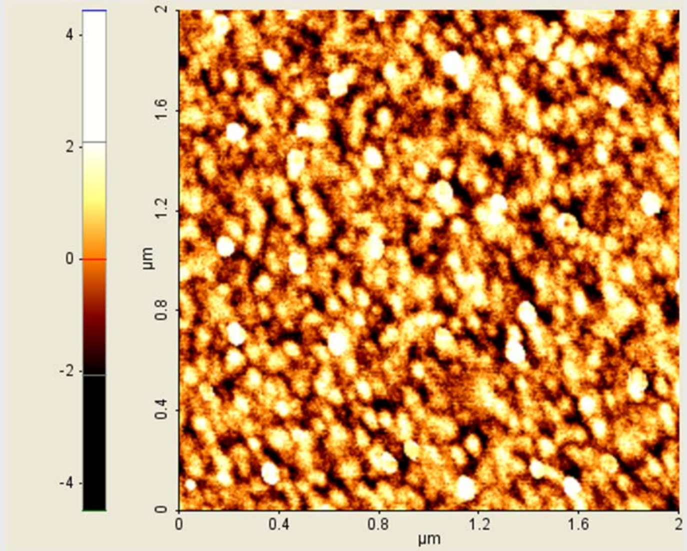
surface effects should not be neglected!!!

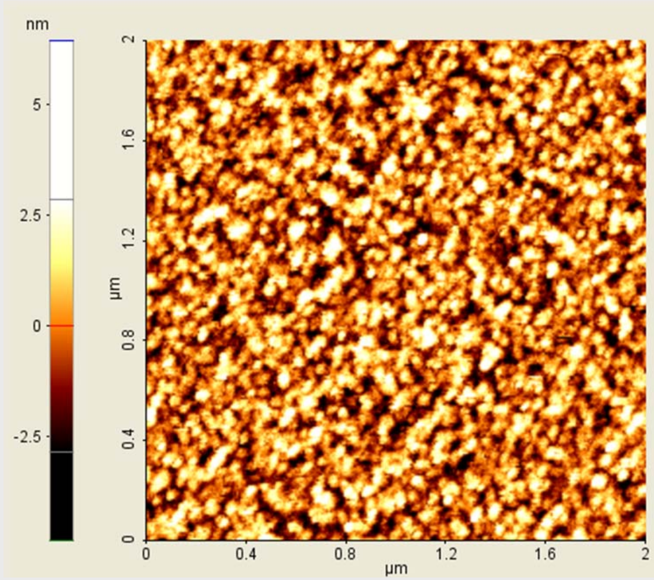


Thick and thin films

- **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



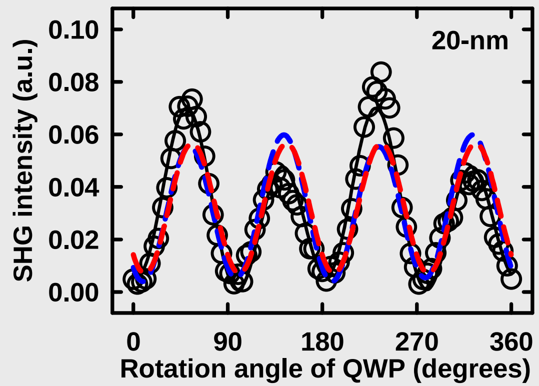




SHG measurements

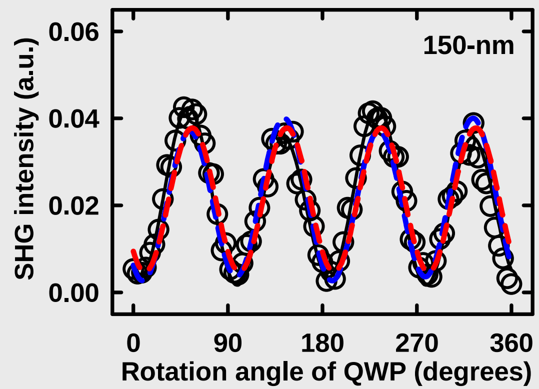
- **s-polarized signals**

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



- **Surface-bulk interference**

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

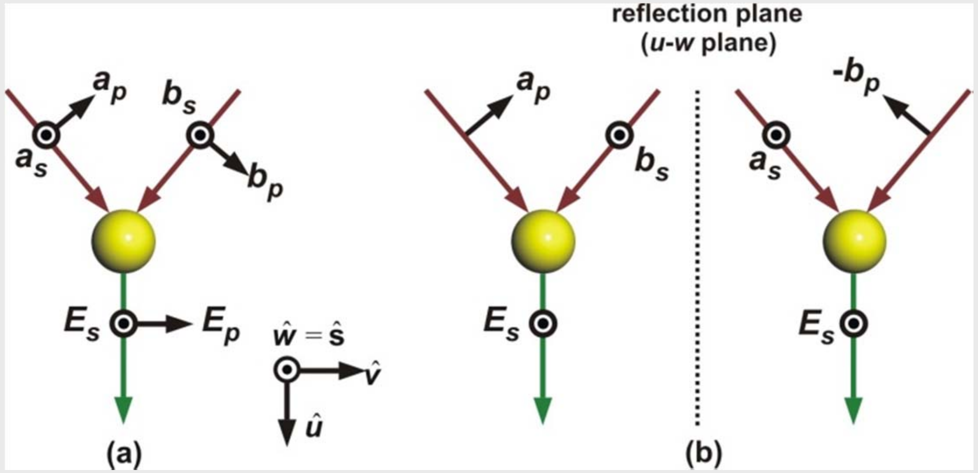


bulk-type response enhanced more by surface roughness

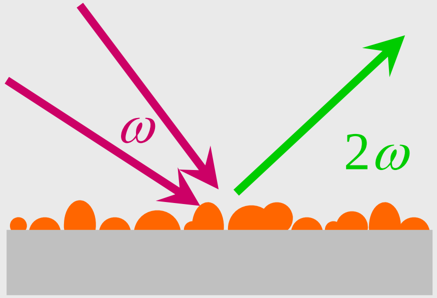
New J. Phys. **12**, 063009 (2010)

Phenomenology

- **Nanoscale feature**
  - idealized to a sphere
- **SHG geometry**
  - two fundamental beams
  - coherent signal

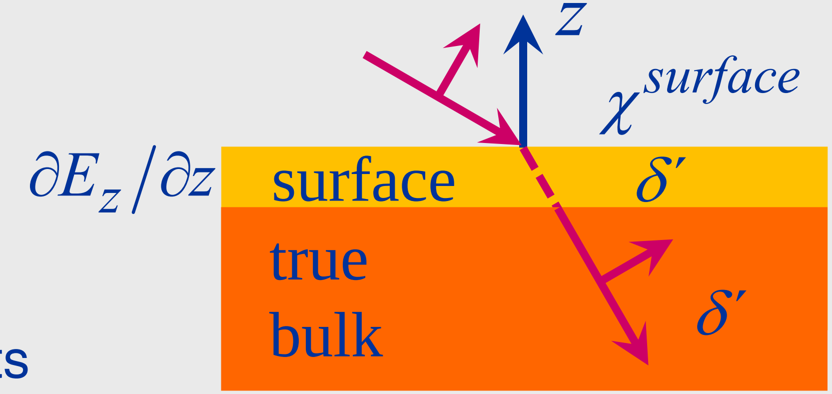


- **Symmetry arguments**
  - different polarizations of the fundamental beams
  - only s-polarized second-harmonic signals allowed
  - behaves as the bulk-type response



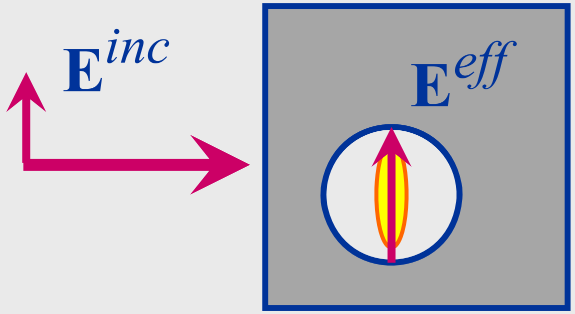
Surface vs. bulk

- **Thin films**
  - surface effects dominate
  - roughness enhances bulk-type response
- **Nanoantennas** [Benedetti, OpEx **19**, 26752 (2011)]
  - relative importance of surface and bulk terms depends on experimental geometry
- **Nanostructures** [Ciraci, PRB **85**, 201403 (2012)]
  - electric mechanism dominates over magnetic
- **Surface contributions**
  - broken surface symmetry
  - bulk terms and surface gradients



Local-field factors

- **Traditional materials**
  - Lorentz local-field factor



$$\boxed{\mathbf{E}^{\mathrm{eff}}(\omega_n) = L(\omega_n)\mathbf{E}^{\mathrm{inc}}(\omega_n)}$$

spectrally flat

- **Effective susceptibility**
  - local-field factors at all frequencies

atomic resonances

$$\boxed{\chi^{\mathrm{eff}}(\omega_1+\omega_2;\omega_1,\omega_2) = L^3\chi^{\mathrm{atomic}}(\omega_1+\omega_2;\omega_1,\omega_2)}$$

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

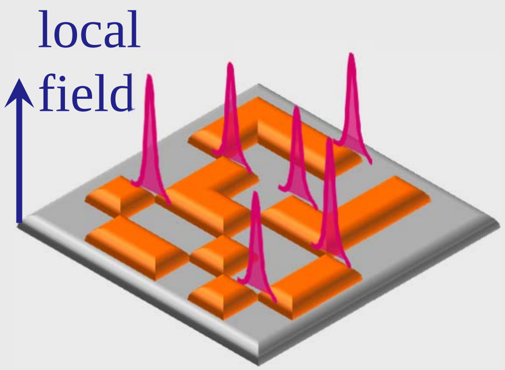
Plasmonic local-field factors

- **Metal structures**
  - tensorial local field factor

Kim, PRB **78**, 113102 (2008)

$$E_i^{\mathrm{eff}}(\omega_n) = L_{ij}(\omega_n) E_j^{\mathrm{inc}}(\omega_n)$$

plasmon resonances



- **Effective nonlinearity**
  - resonant local-field factors

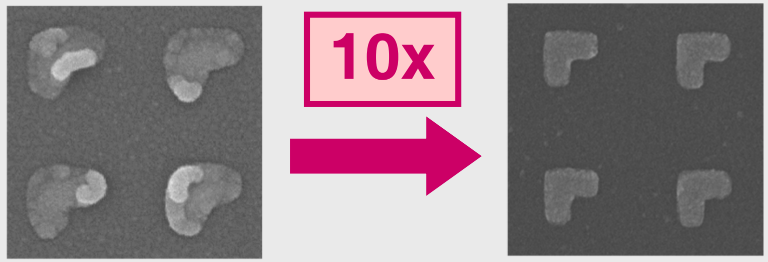
spectrally flat

$$\chi^{\mathrm{eff}}(\omega_1+\omega_2;\omega_1,\omega_2) = \mathbf{L}(\omega_1+\omega_2)\mathbf{L}(\omega_1)\mathbf{L}(\omega_2)\chi^{\mathrm{metal}}$$

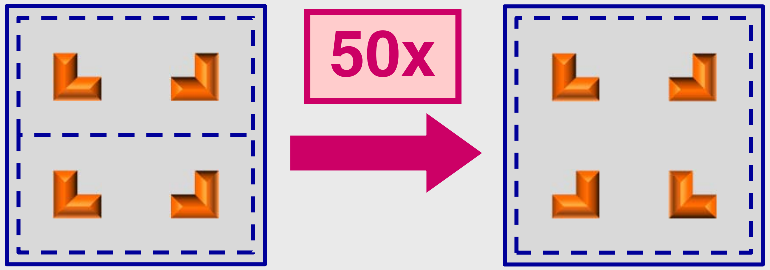
resonances occur in the local-field factors

Improvements in SHG efficiency

- **Sample quality**
  - homogeneous broadening
  - narrow linewidth
  - dipole limit



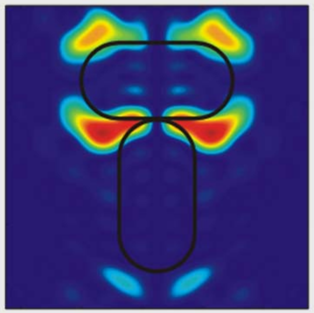
- **Diffractive coupling**
  - particle ordering
  - sharp resonances



- **Passive elements**
  - modification of local modes
  - not optimized yet at all

Towards optimized response

- **Resonance enhancement** [Niesler, OL **36**, 1533 (2011)]
  - fundamental wavelength resonance favorable
  - **SHG resonance, high-order resonances?**
- **Local-field distribution** [Nano Lett. **7**, 1251 (2007)]
  - polarization and asymmetry
  - **surface vs. bulk origin, mode overlap?**



- **Coupling**
  - spectral broadening and narrowing
  - **near-field coupling, photonic coupling?**
- **Multipole effects**
  - **unidirectional SHG?**