Nonlinear optics with metals

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Outline

- **Part II: Second-Order Response of Nanoscale Metals**
  - higher-multipole radiation
  - dipole limit in effective response
  - nanodimers with nanogaps
  - local-field effects

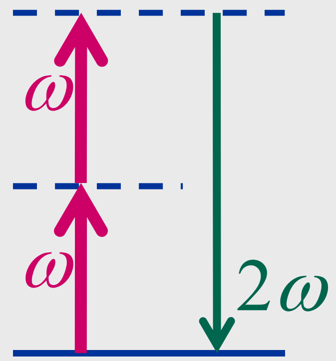
Second-order nonlinear optics

- **Second-order polarization**

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

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

→ **second-harmonic generation**

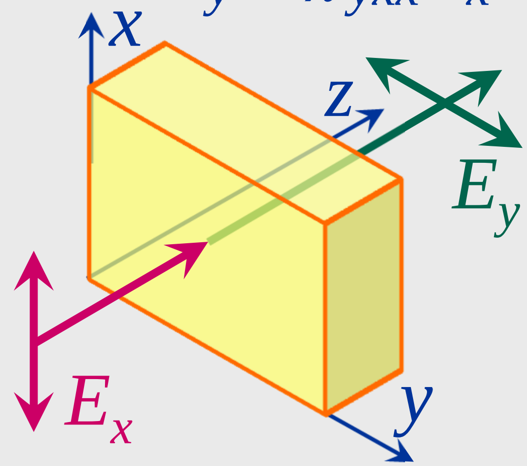


- **Vector quantities** $\mathbf{E}$ $\mathbf{P}$

- **Tensorial response**

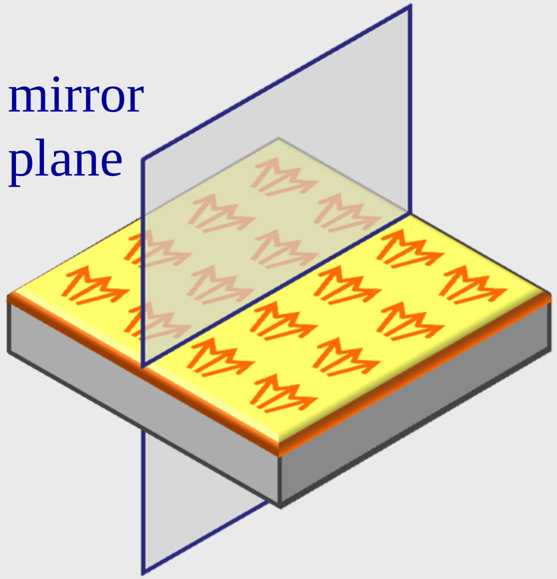
$$P_i = \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k \qquad \mathbf{P} = \boldsymbol{\chi}^{(2)} : \mathbf{EE}$$

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



Symmetry issues

- **Spatial symmetry**
  - symmetry operations
  - interdependent tensor components

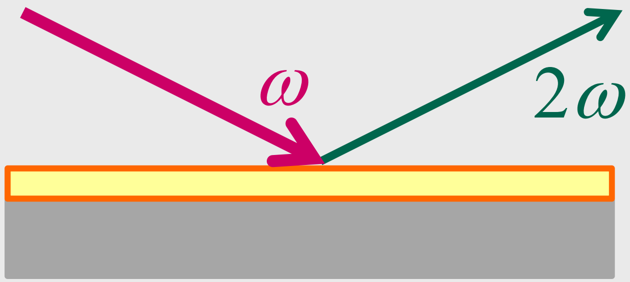


$$\chi^{(2)}_{ijk} \neq 0 \qquad \chi^{(2)}_{ijk} = C\chi^{(2)}_{lmn}$$

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

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

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



Multipole interactions

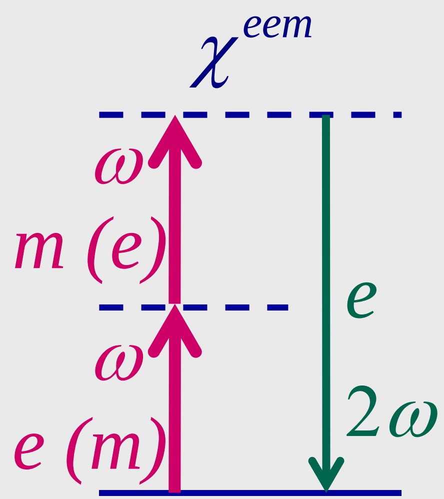
- **Hamiltonian** $H = -\boldsymbol{\mu}\cdot\mathbf{E} - \mathbf{m}\cdot\mathbf{B} - \mathbf{Q}:\nabla\mathbf{E} + \cdots$ **weak**
- **Second-order response**

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

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

- **Magnetic and quadrupole effects**
  – different symmetry properties

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



Multipolar?

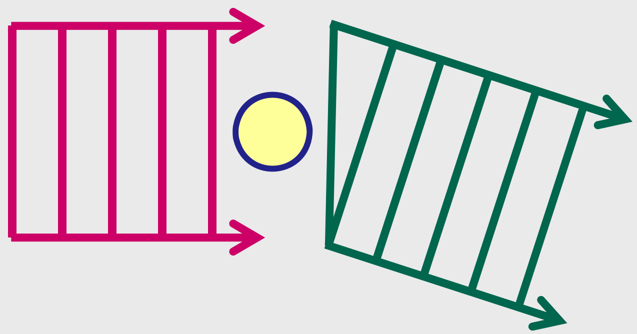
- **Light-matter interaction Hamiltonian**

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

χ^{eee} χ^{eem} χ^{eeQ} χ^{mee} χ^{Qee}

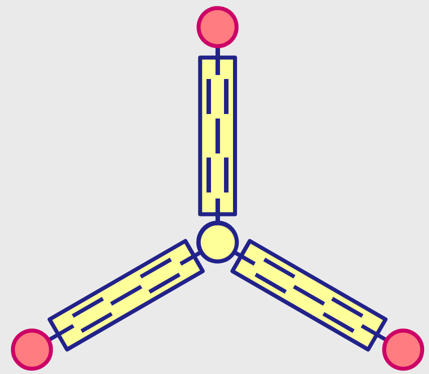
→ **multipolar susceptibilities**

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



→ **Mie-type multipolar radiation patterns**

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



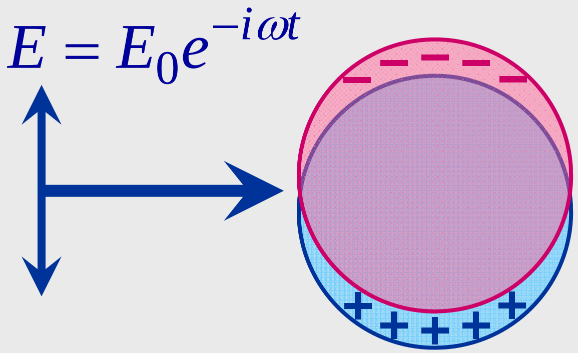
Metal nanoparticles

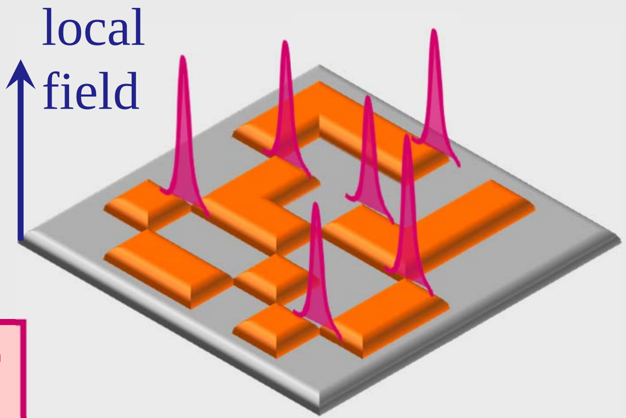
- **Plasmon resonances**
  - collective oscillations of conduction electrons
- **Resonances depend on**
  - size and shape
  - mutual ordering and coupling
  - dielectric environment
- **Nanoscale variations**
  - local fields
  - "hot spots"

  → **enhanced nonlinear response**

  - material properties
  - strong gradients

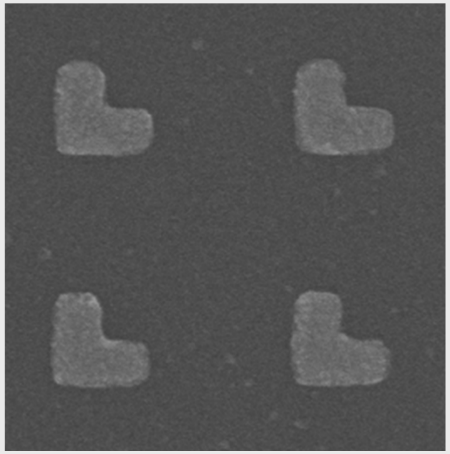
  → **multipole effects**

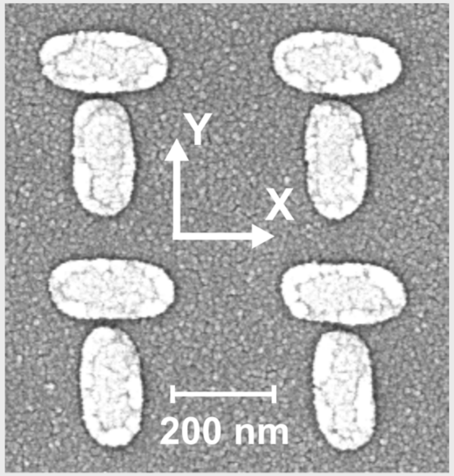




Second-order response

- **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



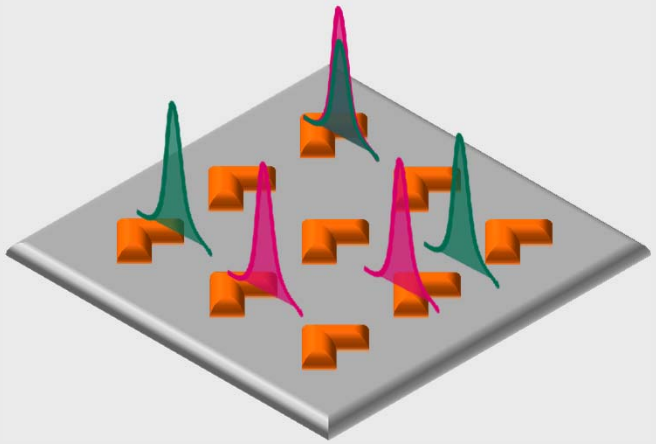


Theoretical descriptions

- **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

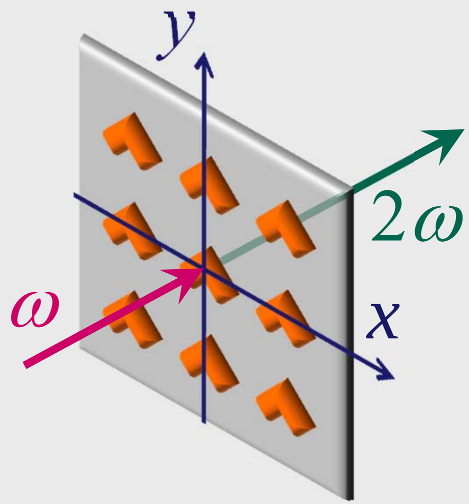
Dadap et al.,
PRL **83**, 4045 (1999)
JOSAB **21**, 1328 (2004)

Nonlinear response tensor

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

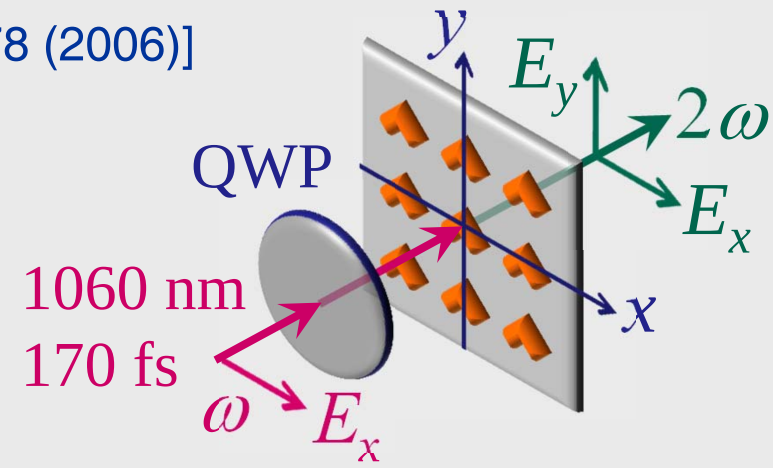
$$E_i(2\omega) = \sum_{j,k} A_{ijk} E_j(\omega) E_k(\omega)$$

- **Disadvantage**
  - specific to experiment, not the sample itself
- **Advantages**
  - avoids nanoscopic difficulties
  - directly measurable quantities
  - all multipoles implicit
  - electric-dipole selection rules
  - equivalent to effective-medium susceptibility



Tensor analysis

- **Fundamental beam** [JOptA **8**, S278 (2006)]
  - QWP modulation of polarization



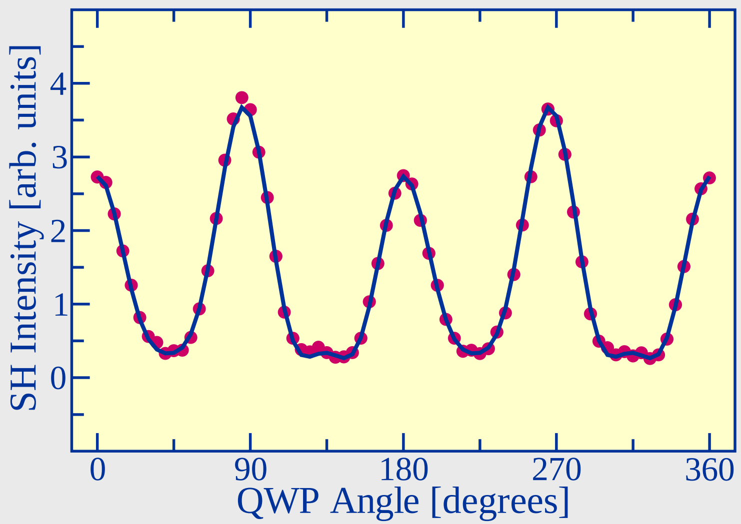
- **Polarized SHG signals**

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

- **Fit coefficients**

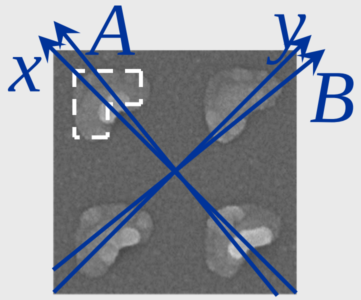
$$f_{x\pm y} = A_{xxx} \pm A_{yxx}$$

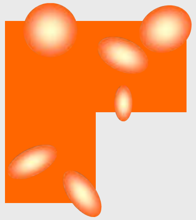
➡ **relative complex values of A_{ijk}**



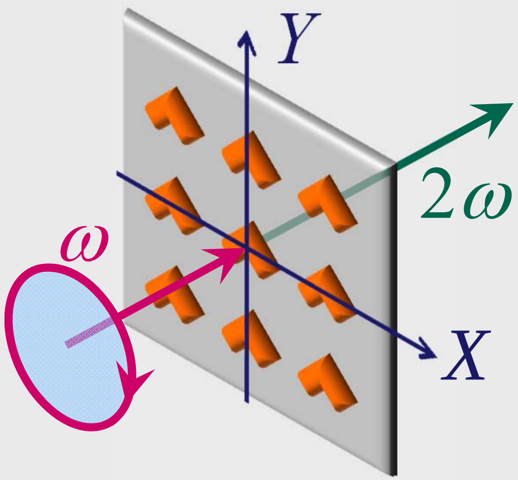
Early results

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

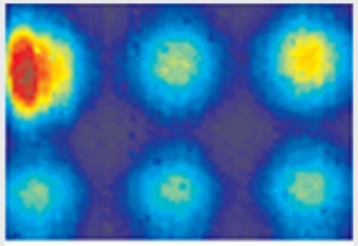




- **Second-harmonic response**
  [Opt. Exp. **12**, 5418 (2004); **14**, 950 (2006)]
  - ”forbidden signals”
  - circular-difference effects
  - chiral symmetry breaking due to defects
  - varying levels of equivalent signals



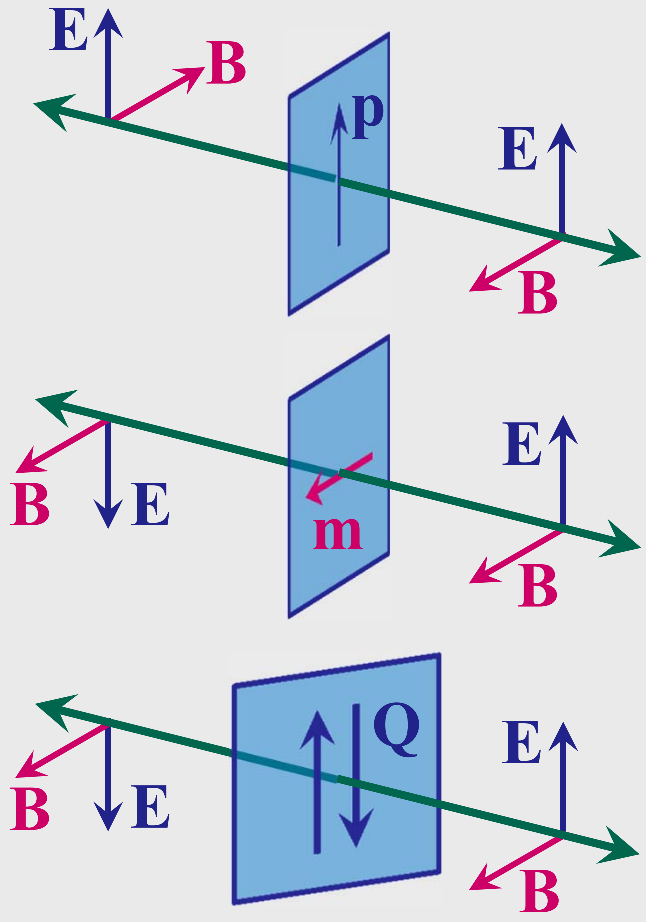
- **Nonlinear microscopy of nanodots**
  [New J. Phys. **10**,013001 (2008)]
  - inhomogeneous tensorial SHG and THG



Multipole effects

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

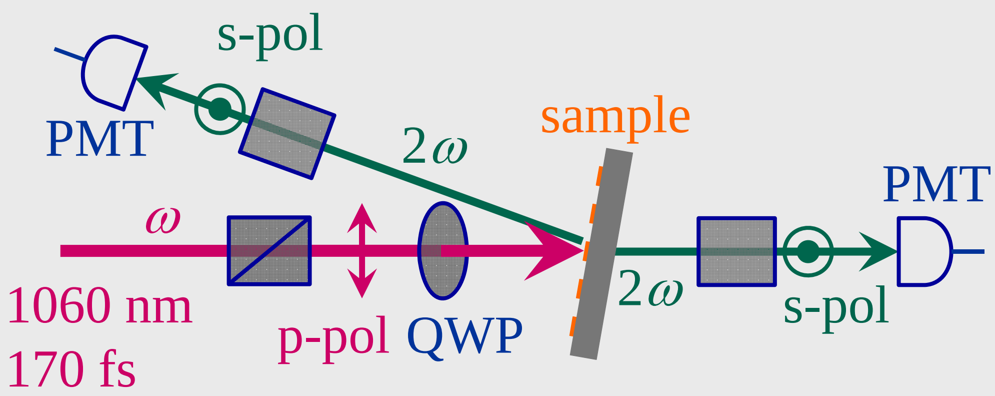
→ **opposite interference in transmission and reflection**



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

Multipole experiment

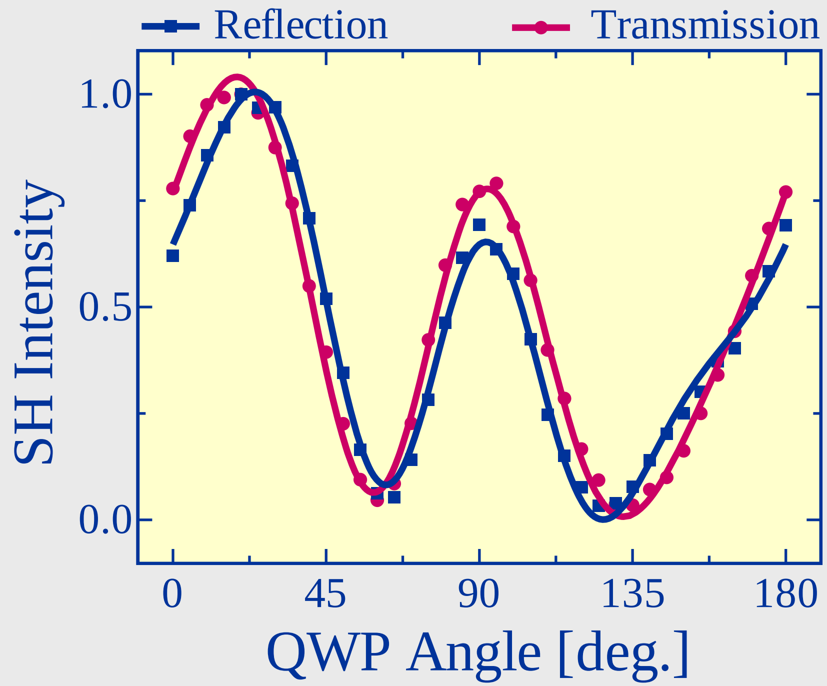
- **Fundamental beam**
  - modulate polarization with quarter-wave plate
  - angle of incidence very small (~1°)



- **Second-harmonic signals**
  - s-polarized detection
  - compare reflected and transmitted lineshapes

clear differences observed

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



Results of tensor analysis

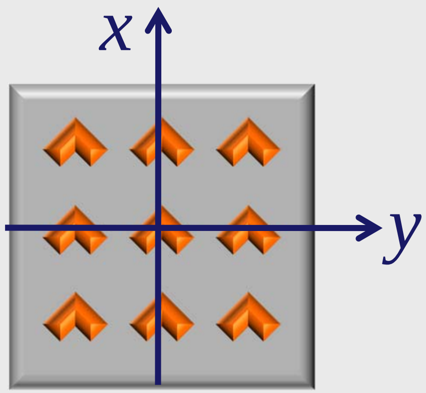
- **Symmetric and antisymmetric parts**

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)



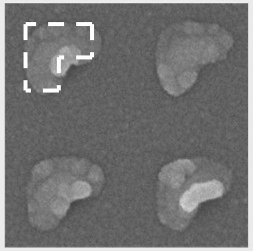
- **Result** [PRL **98**, 167403 (2007)]

	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**

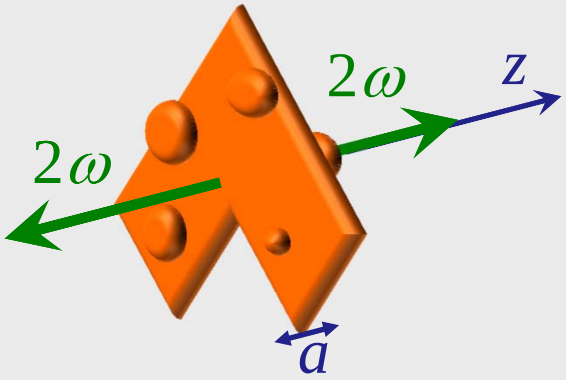
higher multipole amplitude ~20%

Phenomenological model

- **Full tensor analysis**
  [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



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

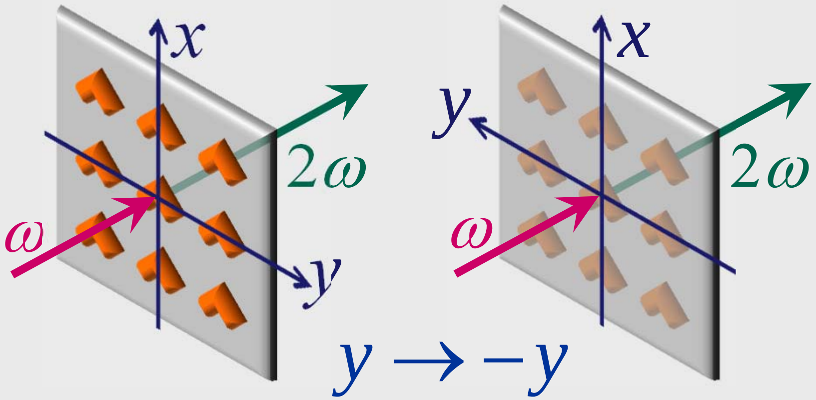
effective dipole

effective quadrupole

Effective multipole tensors

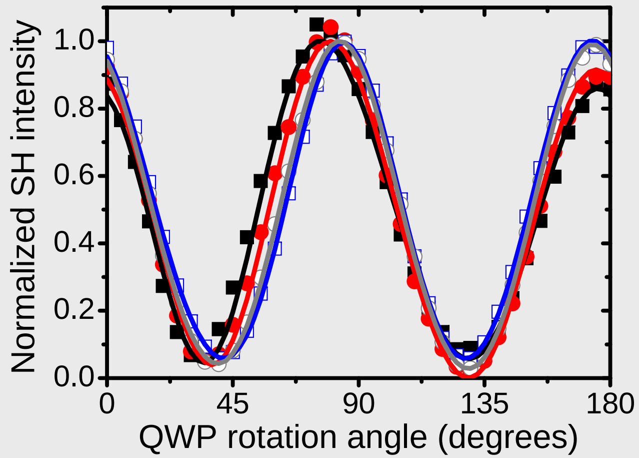
- **Effective dipolar and magnetic tensors**
  [New J. Phys. **13**, 023025 (2011)]

$$A_{xxx} = A^{eee}_{xxx} + A^{eem}_{xxy} + A^{mee}_{yxx}$$



$y \rightarrow -y$

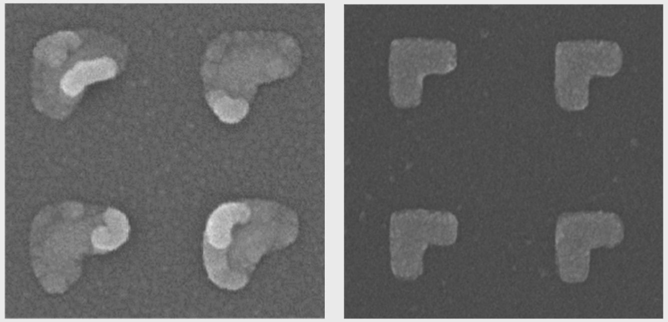
	A^{eee}_{xxx}	A^{eem}_{xxy}	A^{mee}_{yxx}
metal trans.	+	+	+
metal refl.	+	+	-
substrate trans.	+	-	+
substrate refl.	+	-	-



→ **multipolar components about 50% of dipolar components**

New samples

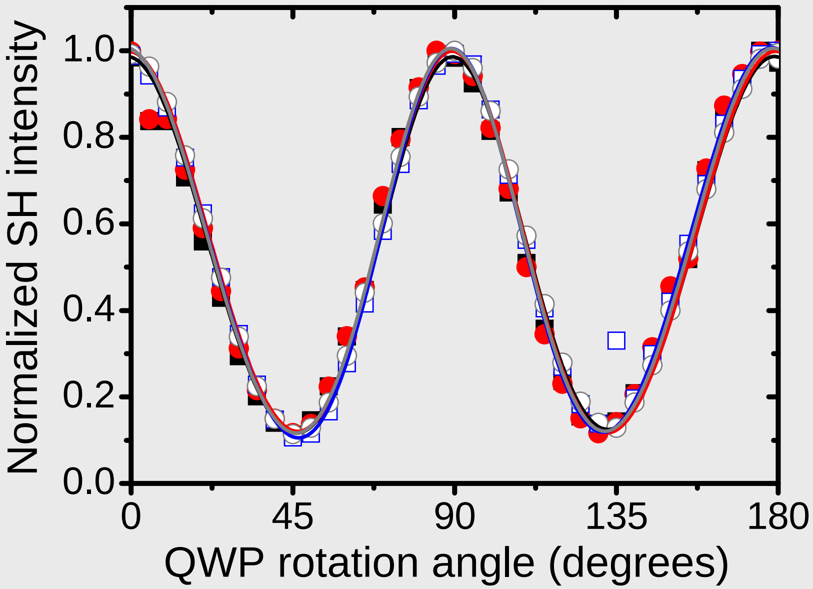
- **Significantly improved quality**
  [Opt. Express **18**, 16601(2010)]
  - narrow extinction peaks
  - high-order resonances observed
  - stronger SHG signals



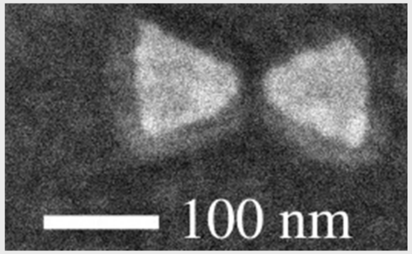
- **Four equivalent signals**
  - all lineshapes overlap

effective dipole limit reached

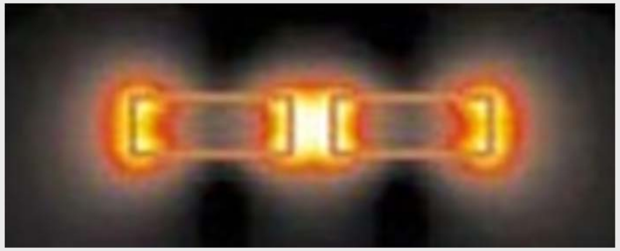
path open for tailorable nonlinear metamaterials



Enhancement in nanogaps

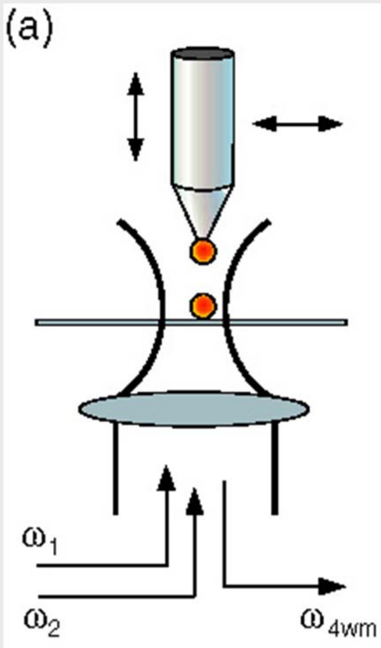


bowtie antenna
[Fromm et al.,Nano Lett. **4**, 957 (2004)]



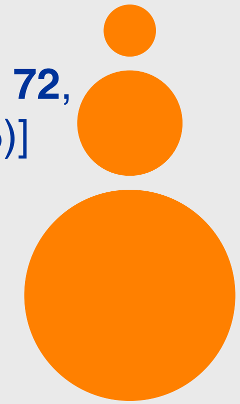
resonant antenna
[Mühlschlegel et al., Science **308**, 1607 (2005)]

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



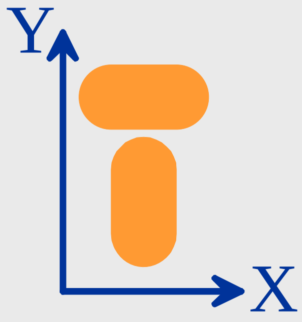
gap-dependent FWM
[Danckwerts and Novotny, PRL **98**, 026104 (2007)]

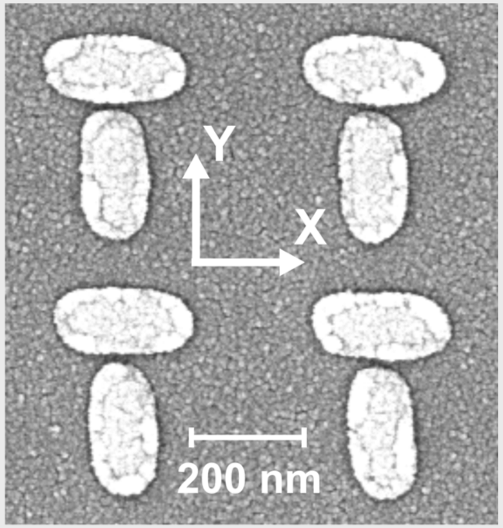
self-similar spheres for SHG
[Li et al., PRB **72**, 153401 (2005)]



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

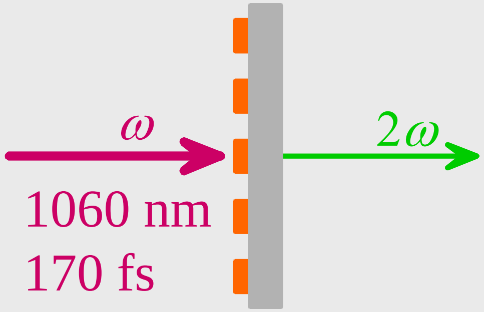


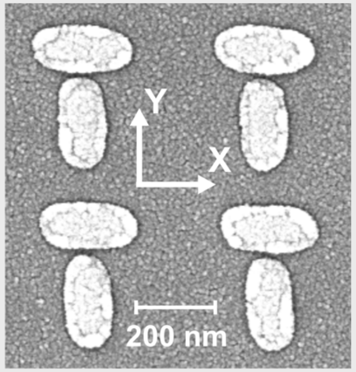


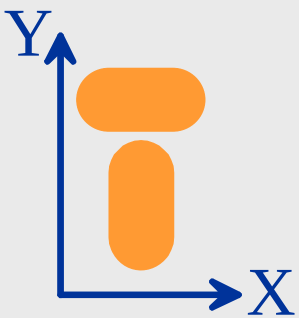
Gap dependence of SHG

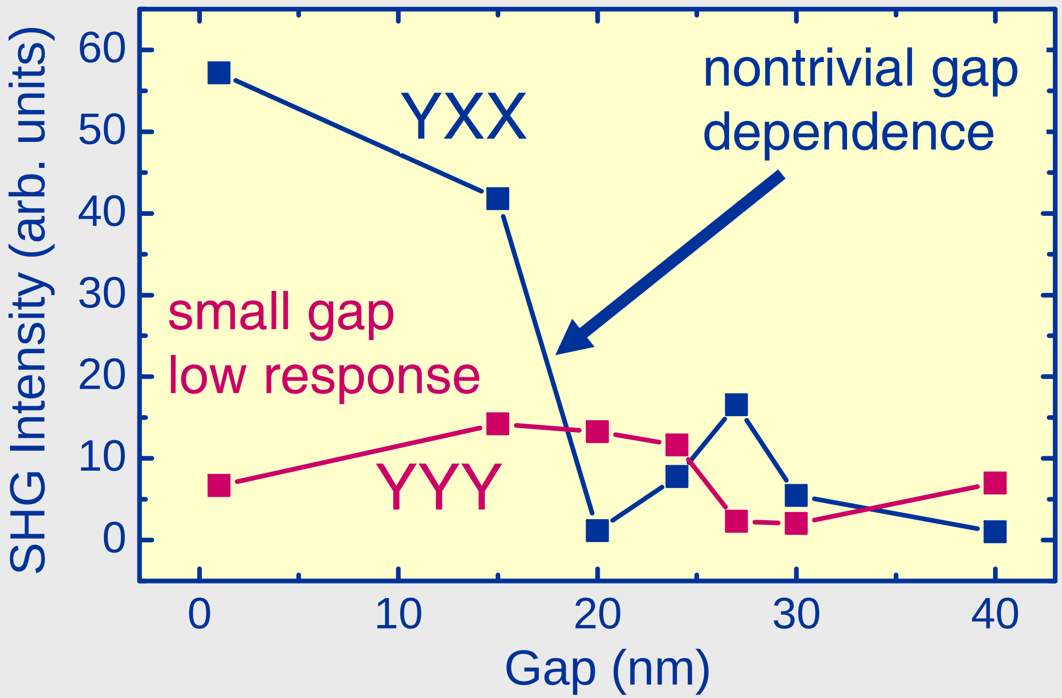
- **SHG signals allowed by symmetry**
  - pure polarization combinations for normal incidence

A_{YXX} , A_{YYY}







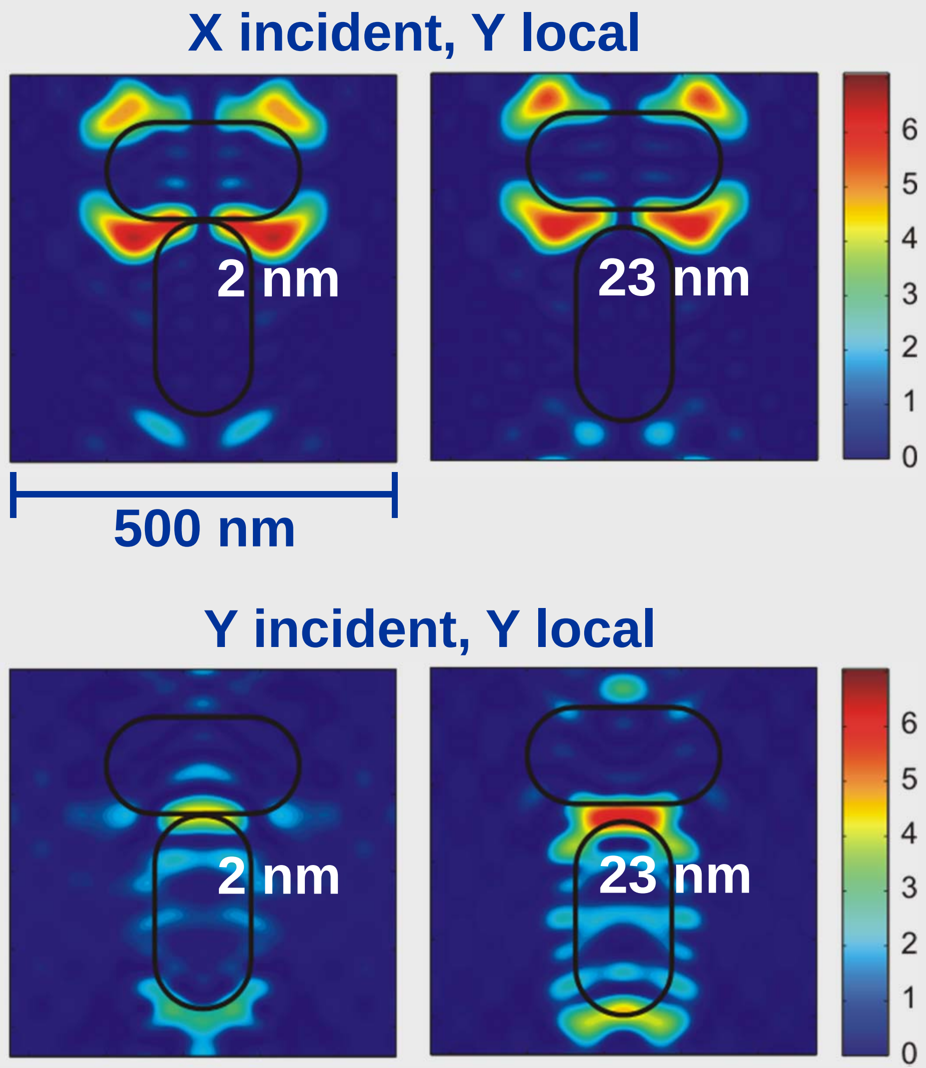


Calculated local-field distributions

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

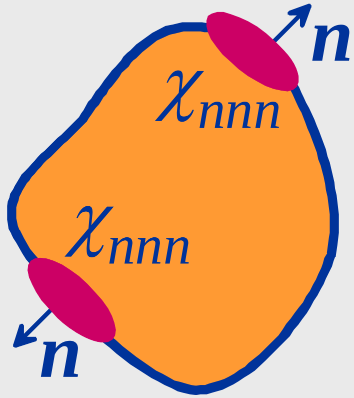
local field contains new polarization components

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



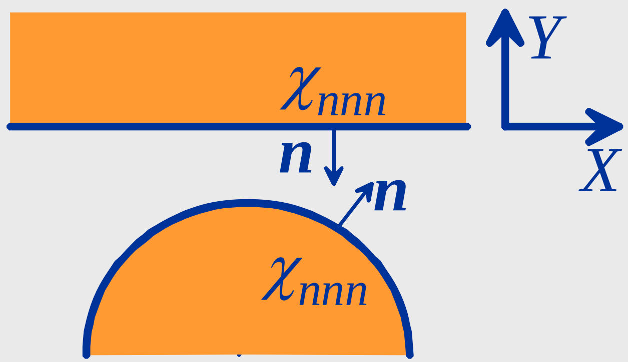
Origin of SHG

- **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

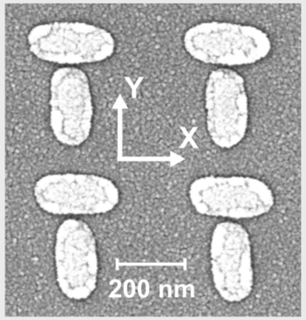


[Nano Lett. **7**, 1251 (2007)]

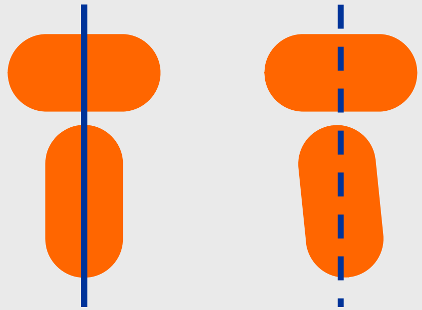
Chiral symmetry breaking

- **Slanted bar orientations**
  - reflection symmetry broken

→ **samples are chiral**

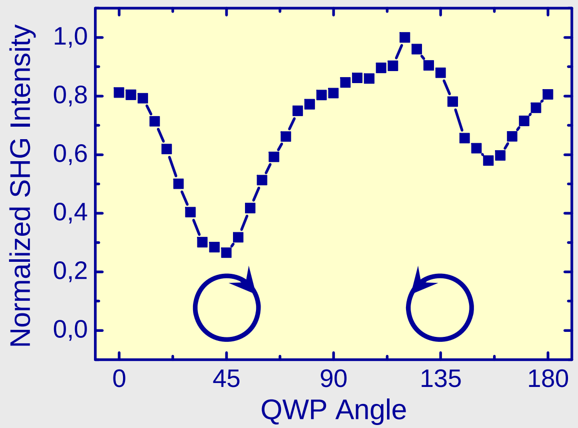


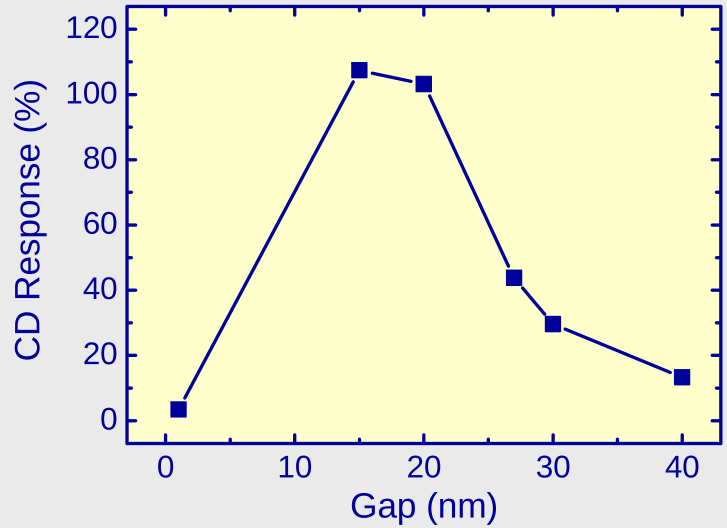
reflection plane



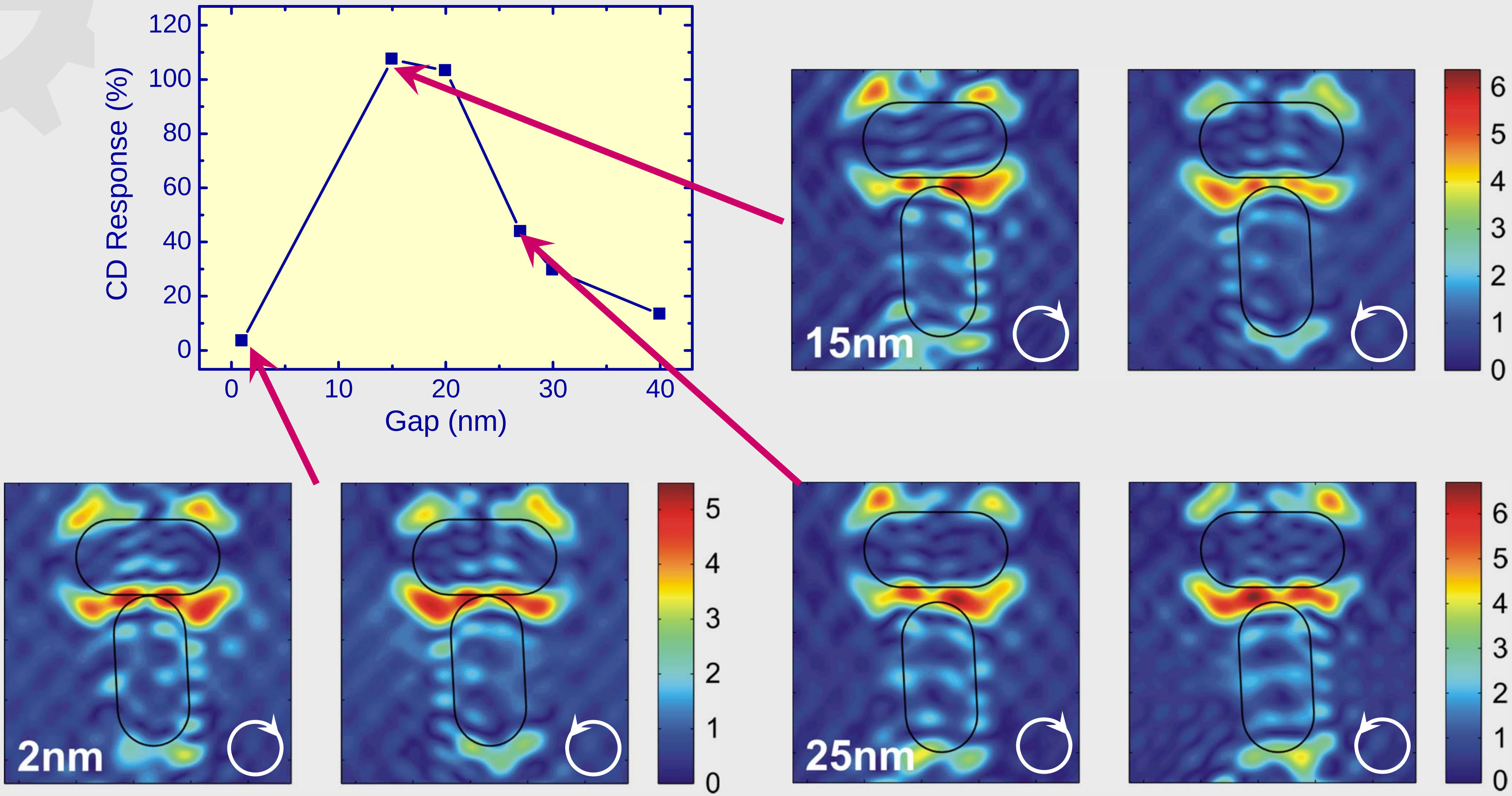
- **Circular-difference response**

$$CDR = 2\frac{I_{LHC} - I_{RHC}}{I_{LHC} + I_{RHC}}$$



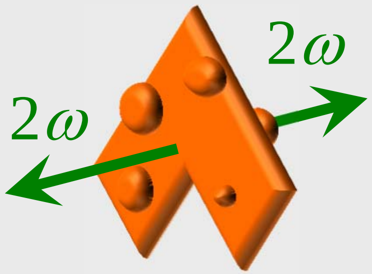


Local-field calculations

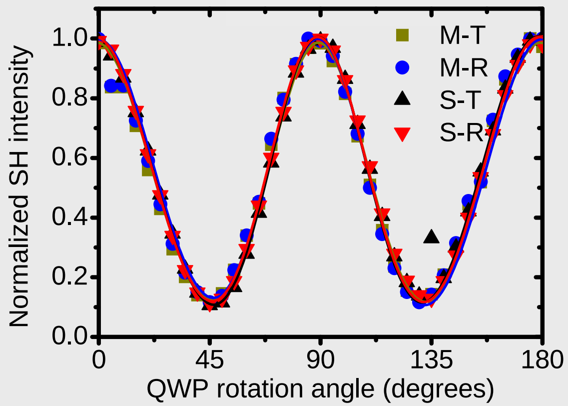


Part II: Conclusions

- **Multipole effects**
  - higher multipoles arise from surface defects



- **Dipole limit reached**
  - improved sample quality
  - multipole effects suppressed
  - prerequisite for nonlinear metamaterials



- **Nanodimers**
  - complicated gap dependence of SHG
  - symmetry and polarization of local fields