Second harmonic generation from nanostructured metal surfaces

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Overview

1. Introduction
2. The importance of symmetry
3. The importance of local field enhancements
   a) Linearly polarized light
   b) Circularly polarized light
4. The road ahead
5. Summary

Overview

Textbooks

- *Principles of nonlinear optics* – Y.R. Shen
- *The elements of nonlinear optics* – Butcher & Cotter
- *Nonlinear optics: basic concepts* – D.L. Mills
- *Nonlinear optics* – R.W. Boyd
- *Handbook of nonlinear optics* – R. L. Sutherland
- *Introduction to nonlinear optical effects in molecules and polymers* – Prassad & Williams

- *Second-order nonlinear optical effects at surfaces and interfaces* – T. F. Heinz, in *Nonlinear Surface Electromagnetic Phenomena* by H. E. Ponath and G. I. Stegeman, eds. (Elsevier, 1991), pp. 353–416
- *Surface second harmonic generation* – P.-F. Brevet
- *Second-Order Nonlinear Optical Characterization Techniques* – T. Verbiest, K. Clays, and V. Rodriguez

- *Symmetry & Magnetism* – R.R. Biriss

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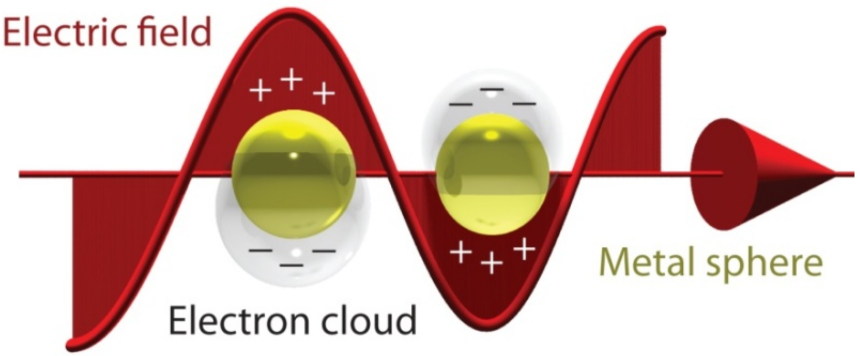
Second Harmonic Generation

In linear optics: $\mathbf{P} = \chi^{(1)} \cdot \mathbf{E}$



For intense electromagnetic fields:

$$\mathbf{P} = \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} : \mathbf{EE} + \chi^{(3)} \vdots \mathbf{EEE} + \ldots$$

The induced polarization contains higher harmonics:

$$\mathbf{P} = \mathbf{P}(0) + \mathbf{P}(\omega) + \mathbf{P}(2\omega) + \mathbf{P}(3\omega) + \ldots$$ where $\mathbf{P}_i(2\omega) = \chi_{ijk}^{(2)} : \mathbf{E}_j(\omega)\mathbf{E}_k(\omega)$

Within the electrical dipole approximation, in centrosymmetric materials:

$$-\mathbf{P}_i(2\omega) = \chi_{ijk}^{(2)} : (-\mathbf{E}_j(\omega))(-\mathbf{E}_k(\omega)) \rightarrow \chi_{ijk}^{(2)} = 0$$

Expending the polarization at 2ω:

The equation $\mathbf{P}_i(2\omega) = \chi^{(2)}_{ijk} : \mathbf{E}_j(\omega)\mathbf{E}_k(\omega)$ can be expanded into:

$$\begin{pmatrix} P_X \\ P_Y \\ P_Z \end{pmatrix} = \begin{pmatrix} \chi_{XXX} & \chi_{XYY} & \chi_{XZZ} & \chi_{XYZ} & \chi_{XXZ} & \chi_{XXY} & \chi_{XZY} & \chi_{XZX} & \chi_{XYX} \\ \chi_{YXX} & \chi_{YYY} & \chi_{YZZ} & \chi_{YYZ} & \chi_{YXZ} & \chi_{YXY} & \chi_{YZY} & \chi_{YZX} & \chi_{YYX} \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & \chi_{ZYZ} & \chi_{ZXZ} & \chi_{ZXY} & \chi_{ZZY} & \chi_{ZZX} & \chi_{ZYX} \end{pmatrix} \begin{pmatrix} E_X E_X \\ E_Y E_Y \\ E_Z E_Z \\ E_Y E_Z \\ E_X E_Z \\ E_X E_Y \\ E_Z E_Y \\ E_Z E_X \\ E_Y E_X \end{pmatrix},$$

where there are way too many tensor components!

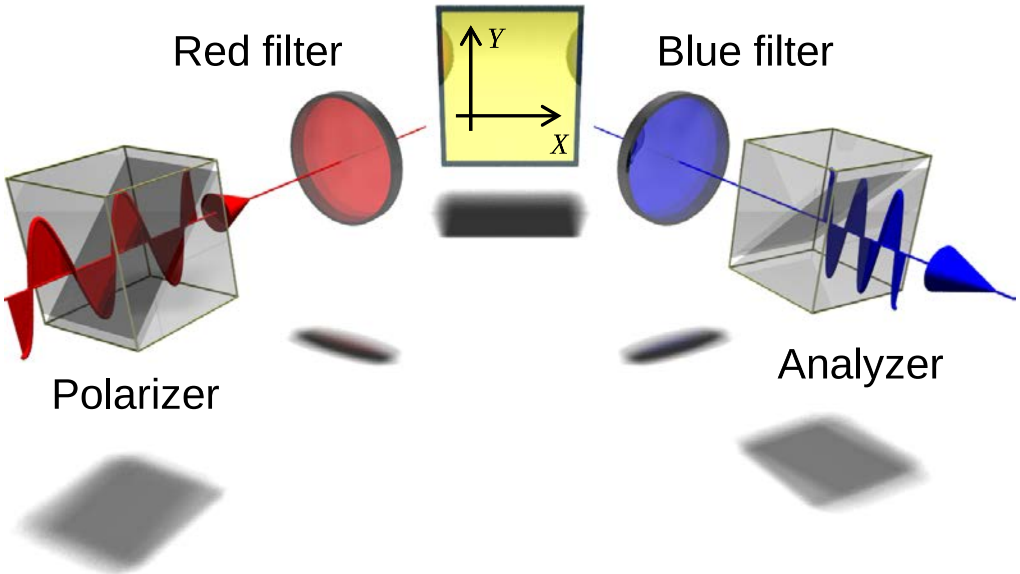
However, because the two electric fields are identical, we have:

$$E_Y E_Z = E_Z E_Y$$
$$E_X E_Z = E_Z E_X$$
$$E_X E_Y = E_Y E_X$$

The meaning of the second harmonic equation

Due to the identity of the electric fields at the fundamental wavelength, the number of independent tensor components diminishes.

$$
\begin{pmatrix} P_X \\ P_Y \\ P_Z \end{pmatrix} = \begin{pmatrix} \chi_{XXX} & \chi_{XYY} & \chi_{XZZ} & \chi_{XYZ} & \chi_{XXZ} & \chi_{XXY} \\ \chi_{YXX} & \chi_{YYY} & \chi_{YZZ} & \chi_{YYZ} & \chi_{YXZ} & \chi_{YXY} \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & \chi_{ZYZ} & \chi_{ZXZ} & \chi_{ZXY} \end{pmatrix} \begin{pmatrix} E_X^2 \\ E_Y^2 \\ E_Z^2 \\ 2E_Y E_Z \\ 2E_X E_Z \\ 2E_X E_Y \end{pmatrix},
$$

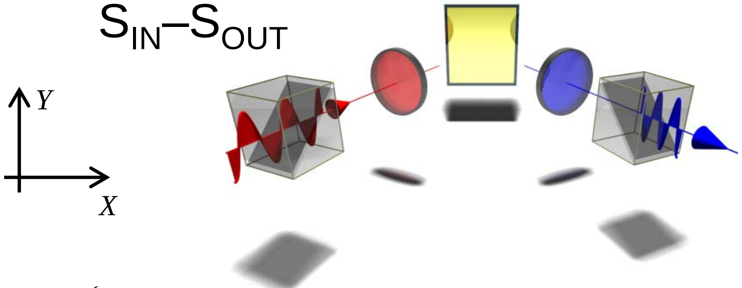


Specific tensor components can be addressed by selecting certain polarizer-analyzer combinations.

How does this work exactly?

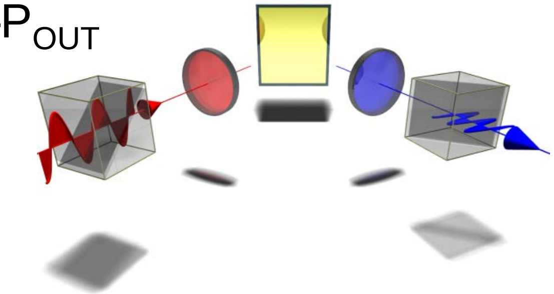
Tensor components depending on polarization

S_{IN}–S_{OUT}



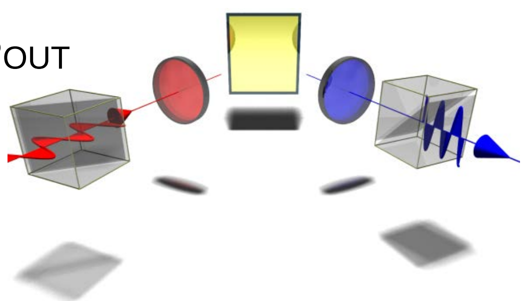
$$\begin{pmatrix} \chi_{XXX} & \chi_{XYY} & \chi_{XZZ} & \chi_{XYZ} & \chi_{XXZ} & \chi_{XXY} \\ \chi_{YXX} & \color{blue}{\chi_{YYY}} & \chi_{YZZ} & \chi_{YYZ} & \chi_{YXZ} & \chi_{YXY} \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & \chi_{ZYZ} & \chi_{ZXZ} & \chi_{ZXY} \end{pmatrix}$$

S_{IN}–P_{OUT}



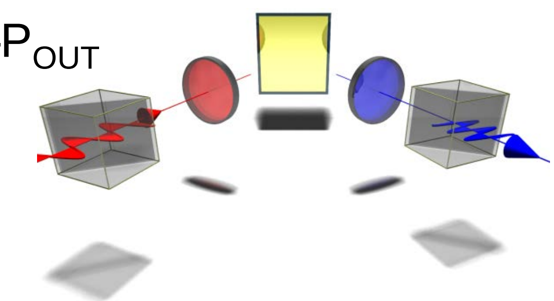
$$\begin{pmatrix} \chi_{XXX} & \color{blue}{\chi_{XYY}} & \chi_{XZZ} & \chi_{XYZ} & \chi_{XXZ} & \chi_{XXY} \\ \chi_{YXX} & \chi_{YYY} & \chi_{YZZ} & \chi_{YYZ} & \chi_{YXZ} & \chi_{YXY} \\ \chi_{ZXX} & \color{blue}{\chi_{ZYY}} & \chi_{ZZZ} & \chi_{ZYZ} & \chi_{ZXZ} & \chi_{ZXY} \end{pmatrix}$$

P_{IN}–S_{OUT}



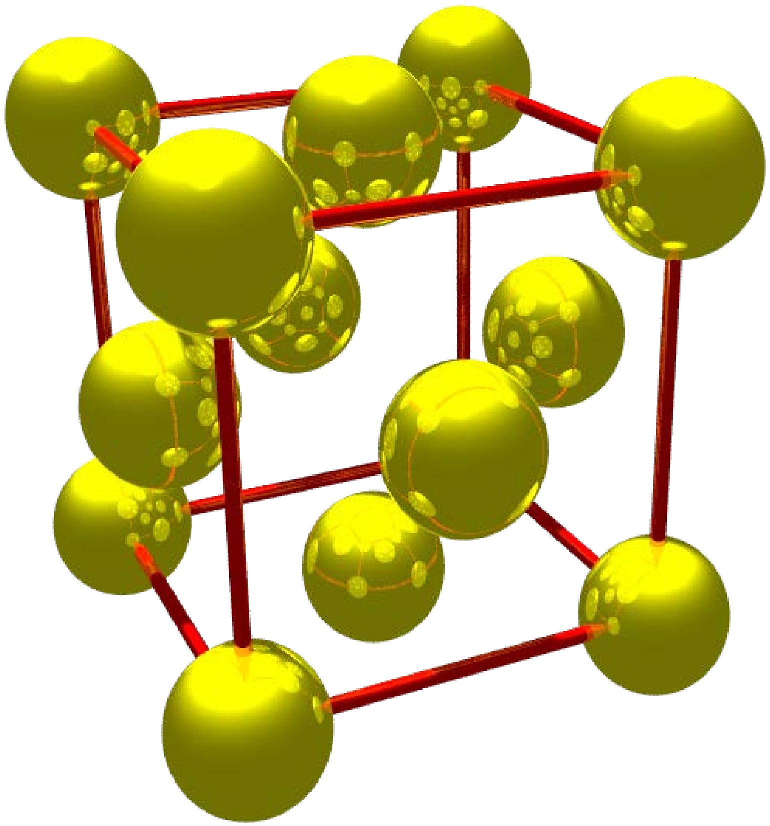
$$\begin{pmatrix} \chi_{XXX} & \chi_{XYY} & \chi_{XZZ} & \chi_{XYZ} & \chi_{XXZ} & \chi_{XXY} \\ \color{blue}{\chi_{YXX}} & \chi_{YYY} & \color{blue}{\chi_{YZZ}} & \chi_{YYZ} & \color{blue}{\chi_{YXZ}} & \chi_{YXY} \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & \chi_{ZYZ} & \chi_{ZXZ} & \chi_{ZXY} \end{pmatrix}$$

P_{IN}–P_{OUT}



$$\begin{pmatrix} \color{blue}{\chi_{XXX}} & \chi_{XYY} & \color{blue}{\chi_{XZZ}} & \chi_{XYZ} & \color{blue}{\chi_{XXZ}} & \chi_{XXY} \\ \chi_{YXX} & \chi_{YYY} & \chi_{YZZ} & \chi_{YYZ} & \chi_{YXZ} & \chi_{YXY} \\ \color{blue}{\chi_{ZXX}} & \chi_{ZYY} & \color{blue}{\chi_{ZZZ}} & \chi_{ZYZ} & \color{blue}{\chi_{ZXZ}} & \chi_{ZXY} \end{pmatrix}$$

Gold has a face centered cubic crystal structure



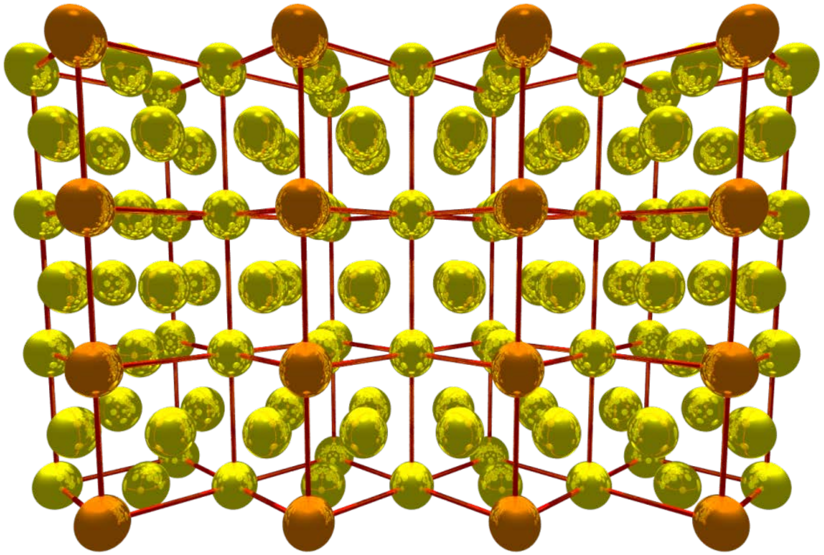
Other metals with this crystal structure are: Al, Cu, Ni, Sr, Rh, Pd, Ag, Ce, Tb, Ir, Pt, Pb and Th.

Depending on the direction of cleaving, the Au crystal surface can exhibit 2-fold, 3-fold and 4-fold symmetry.

These symmetries are revealed by arranging the cubes.

In what way do these symmetries affect the SHG signal?

The (110) surface of gold has 2-fold symmetry



$$\text{2-fold symmetry:}\begin{cases} X \to -X \\ Y \to -Y \end{cases}$$

$$\begin{pmatrix} XXX & XYY & XZZ & XYZ & XXZ & XXY \\ YXX & YYY & YZZ & YYZ & YXZ & YXY \\ ZXX & ZYY & ZZZ & ZYZ & ZXZ & ZXY \end{pmatrix}$$

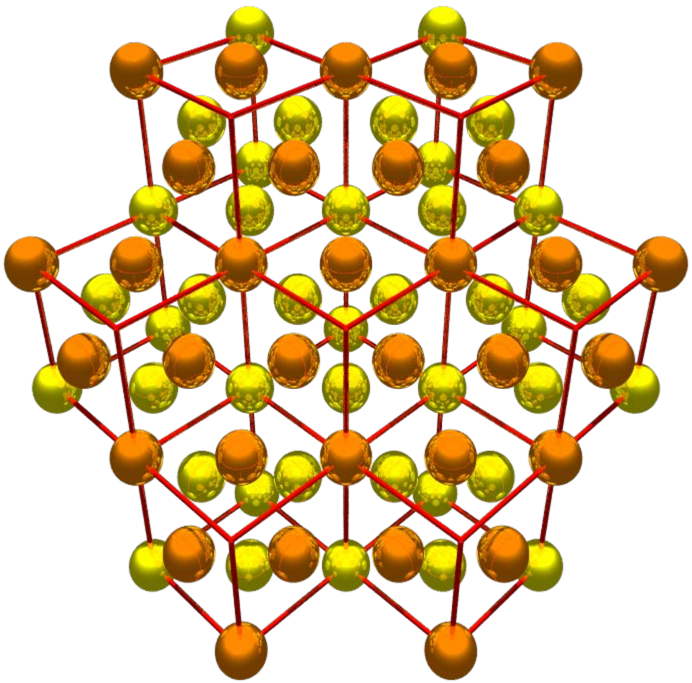
$$XXX \overbrace{=}^{\substack{X \to -X \\ Y \to -Y}} (-X)(-X)(-X) = -XXX = 0$$

$$\begin{pmatrix} 0 & XYY & XZZ & XYZ & XXZ & XXY \\ YXX & YYY & YZZ & YYZ & YXZ & YXY \\ ZXX & ZYY & ZZZ & ZYZ & ZXZ & ZXY \end{pmatrix}$$

$$ZXX \overbrace{=}^{\substack{X \to -X \\ Y \to -Y}} Z(-X)(-X) = ZXX \neq 0$$

$$\begin{pmatrix} 0 & XYY & XZZ & XYZ & XXZ & XXY \\ YXX & YYY & YZZ & YYZ & YXZ & YXY \\ \color{blue}{ZXX} & ZYY & ZZZ & ZYZ & ZXZ & ZXY \end{pmatrix}$$

The (111) surface of gold has 3-fold symmetry

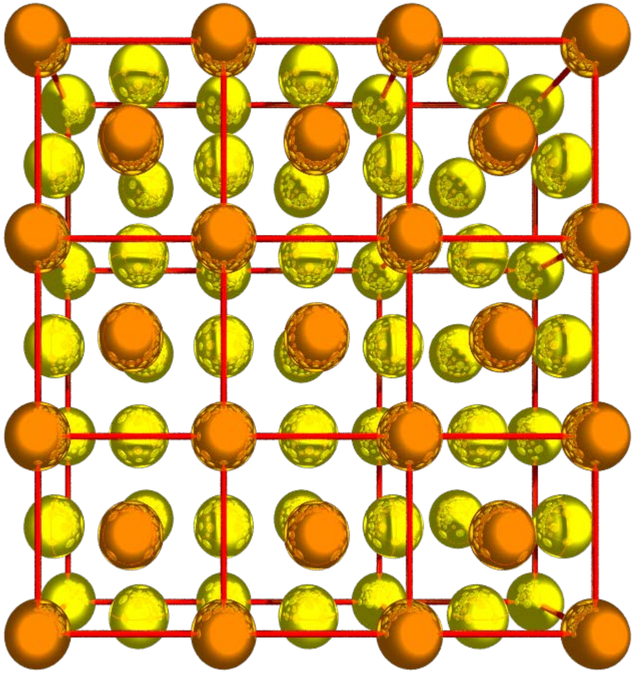


$$\text{3-fold symmetry:}\begin{cases} X \to -\frac{1}{2}X + \frac{\sqrt{3}}{2}Y \\ X \to -\frac{1}{2}X - \frac{\sqrt{3}}{2}Y \end{cases}$$

$$\begin{pmatrix} XXX & XYY & XZZ & XYZ & XXZ & XXY \\ YXX & YYY & YZZ & YYZ & YXZ & YXY \\ ZXX & ZYY & ZZZ & ZYZ & ZXZ & ZXY \end{pmatrix}$$

$$\left.\begin{array}{ll} ZXZ = Z\left(-\frac{1}{2}X + \frac{\sqrt{3}}{2}Y\right)Z = -\frac{1}{2}ZXZ + \frac{\sqrt{3}}{2}ZYZ & \therefore \frac{3}{2}ZXZ = \frac{\sqrt{3}}{2}ZYZ \\ ZXZ = Z\left(-\frac{1}{2}X - \frac{\sqrt{3}}{2}Y\right)Z = -\frac{1}{2}ZXZ - \frac{\sqrt{3}}{2}ZYZ & \therefore \frac{3}{2}ZXZ = -\frac{\sqrt{3}}{2}ZYZ \end{array}\right\} \therefore ZXZ = ZYZ = 0$$

The (001) surface of gold has 4-fold symmetry

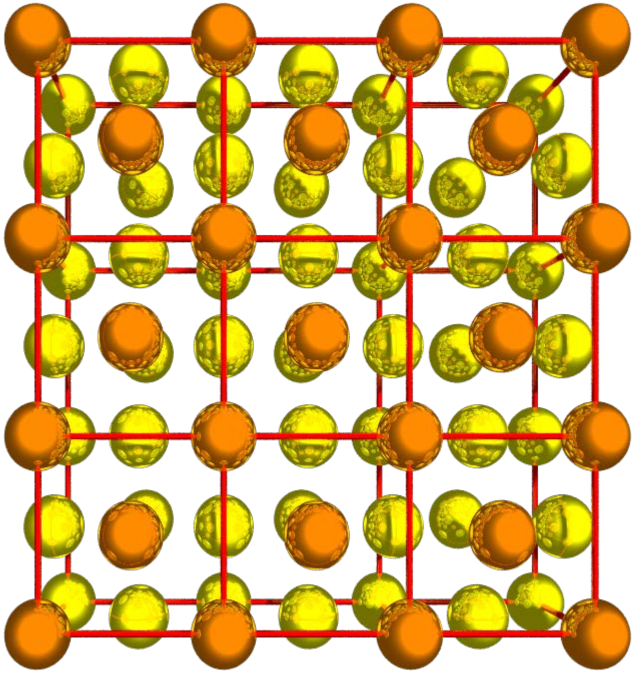


4-fold symmetry: $\begin{cases} X \rightarrow +Y \\ Y \rightarrow -X \end{cases}$

$$\begin{pmatrix} XXX & XYY & XZZ & XYZ & XXZ & XXY \\ YXX & YYY & YZZ & YYZ & YXZ & YXY \\ ZXX & ZYY & ZZZ & ZYZ & ZXZ & ZXY \end{pmatrix}$$

A 4-fold symmetric surface also allows the 2-fold symmetry.

The (001) surface of gold has 4-fold symmetry



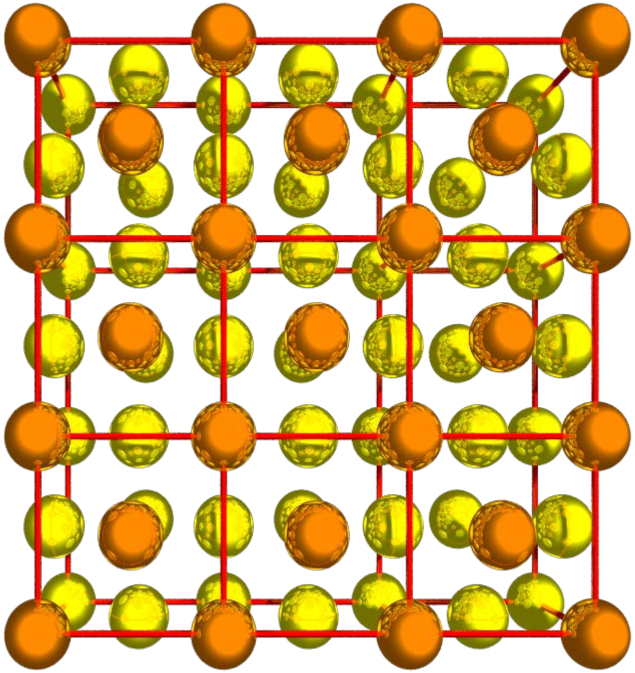
$$\text{4-fold symmetry:}\begin{cases} X \to +Y \\ Y \to -X \end{cases}$$

$$\begin{pmatrix} XXX & XYY & XZZ & XYZ & XXZ & XXY \\ YXX & YYY & YZZ & YYZ & YXZ & YXY \\ ZXX & ZYY & ZZZ & ZYZ & ZXZ & ZXY \end{pmatrix}$$

All tensor components with odd number of either X or Y indices are 0.

$$\begin{pmatrix} 0 & 0 & 0 & XYZ & XXZ & 0 \\ 0 & 0 & 0 & XXZ & -XYZ & 0 \\ ZXX & ZXX & ZZZ & 0 & 0 & \color{red}{0} \end{pmatrix}$$

The (001) surface of gold has mirror symmetry



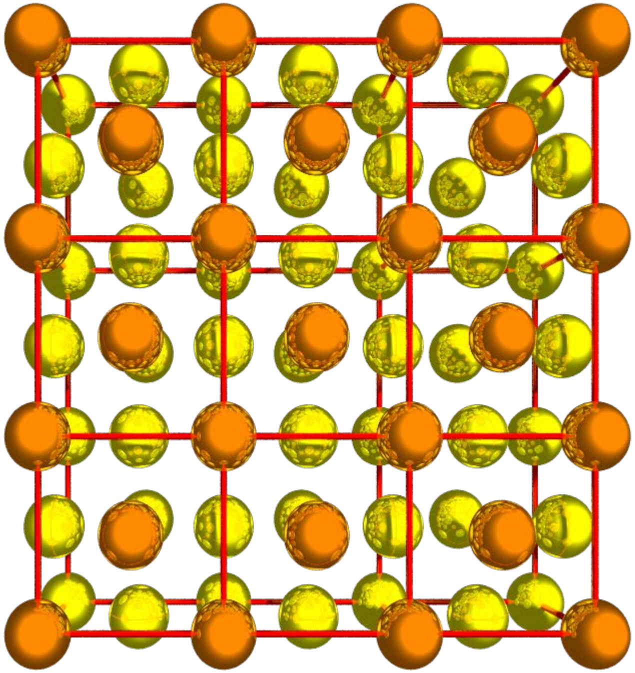
$$\mathrm{m} \perp Y,\ \text{mirror symmetry:}\begin{cases} X \to +X \\ Y \to -Y \end{cases}$$

$$\mathrm{m} \perp X,\ \text{mirror symmetry:}\begin{cases} X \to -X \\ Y \to +Y \end{cases}$$

All tensor components with odd number of X or Y indices are 0. No relationship between tensor components.

$$\begin{pmatrix} 0 & 0 & 0 & 0 & XXZ & 0 \\ 0 & 0 & 0 & YYZ & 0 & 0 \\ ZXX & ZYY & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

The (001) surface of gold has both 4-fold and mirror symmetry



4-fold:

$$\begin{pmatrix} 0 & 0 & 0 & XYZ & XXZ & 0 \\ 0 & 0 & 0 & XXZ & -XYZ & 0 \\ ZXX & ZXX & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

mirrors:

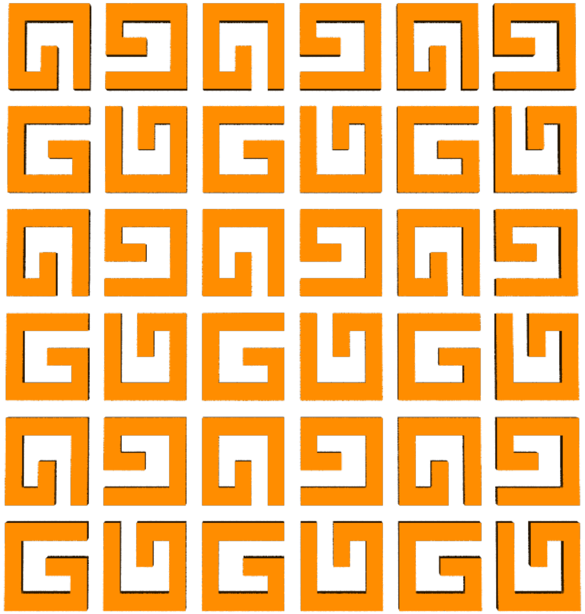
$$\begin{pmatrix} 0 & 0 & 0 & 0 & XXZ & 0 \\ 0 & 0 & 0 & YYZ & 0 & 0 \\ ZXX & ZYY & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

The mirror symmetry is more restrictive than the 4-fold one. The latter gives us the relations between tensor components.

The tensor for the (001) surface:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & XXZ & 0 \\ 0 & 0 & 0 & XXZ & 0 & 0 \\ ZXX & ZXX & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

The 4-fold chiral surface



4-fold:

$$\begin{pmatrix} 0 & 0 & 0 & XYZ & XXZ & 0 \\ 0 & 0 & 0 & XXZ & -XYZ & 0 \\ ZXX & ZXX & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

mirrors:

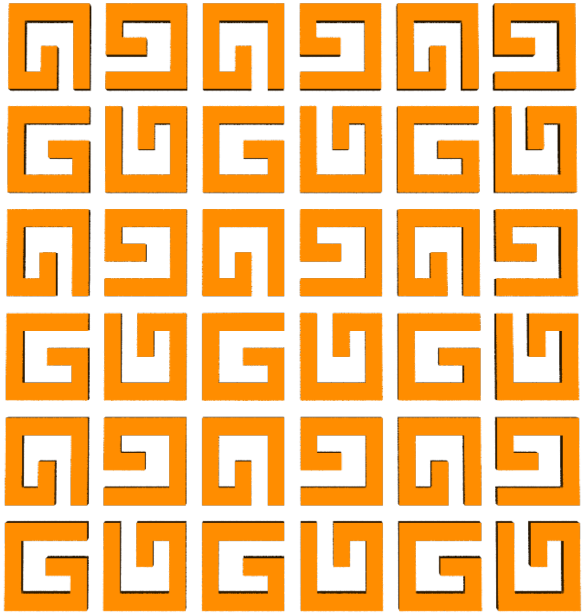
$$\begin{pmatrix} 0 & 0 & 0 & 0 & XXZ & 0 \\ 0 & 0 & 0 & YYZ & 0 & 0 \\ ZXX & ZYY & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

The mirror symmetry is more restrictive than the 4-fold one. The latter gives us the relations between tensor components.

The tensor for the (001) surface:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & XXZ & 0 \\ 0 & 0 & 0 & XXZ & 0 & 0 \\ ZXX & ZXX & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

The 4-fold chiral surface



4-fold:

$$\begin{pmatrix} 0 & 0 & 0 & XYZ & XXZ & 0 \\ 0 & 0 & 0 & XXZ & -XYZ & 0 \\ ZXX & ZXX & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

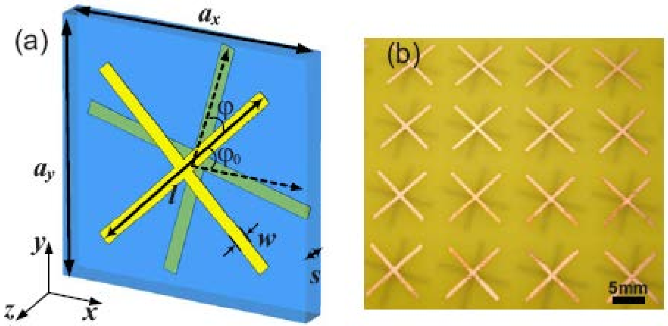
mirrors:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & XXZ & 0 \\ 0 & 0 & 0 & YYZ & 0 & 0 \\ ZXX & ZYY & ZZZ & 0 & 0 & 0 \end{pmatrix}$$

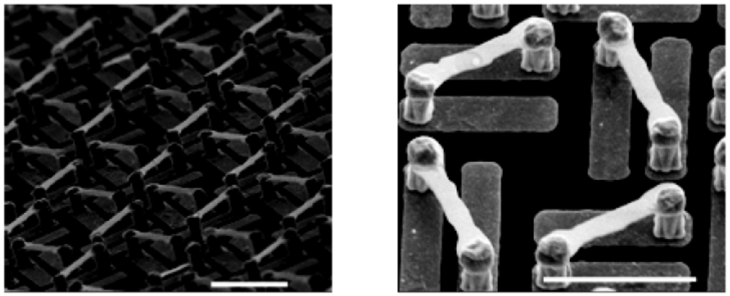
By definition, a chiral surface lacks mirror planes.

In fact there is a variety of nanostructured geometries that are chiral.

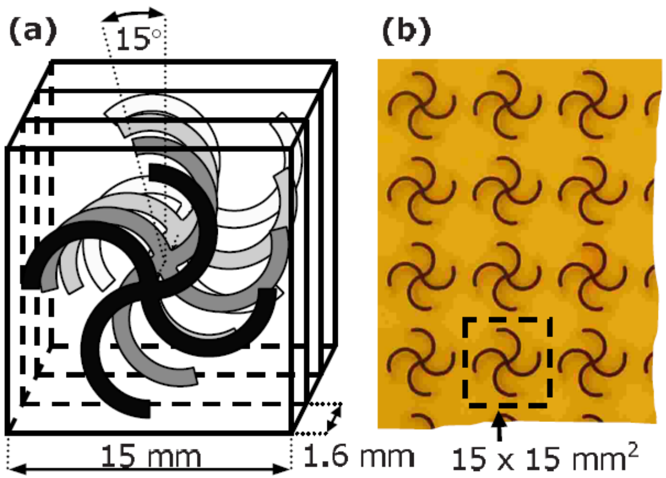
Chirality and negative refractive index



J. Zhou, J. Dong, B. Wang, T. Koschny, M. Kafesaki, and C. M. Soukoulis, Phys. Rev. B **79**, 121104(R) (2009).

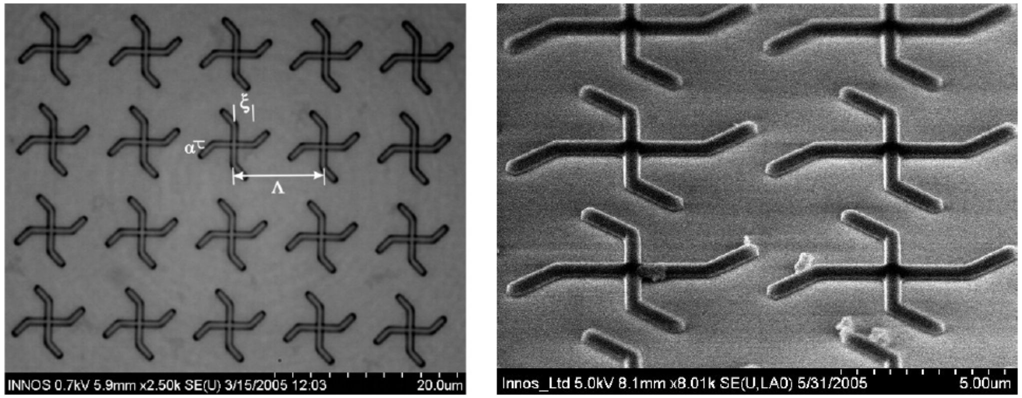


S. Zhang, Y.S. Park, J. Li, X. Lu, W. Zhang, and X. Zhang, Phys. Rev. Lett. **102**, 023901 (2009).

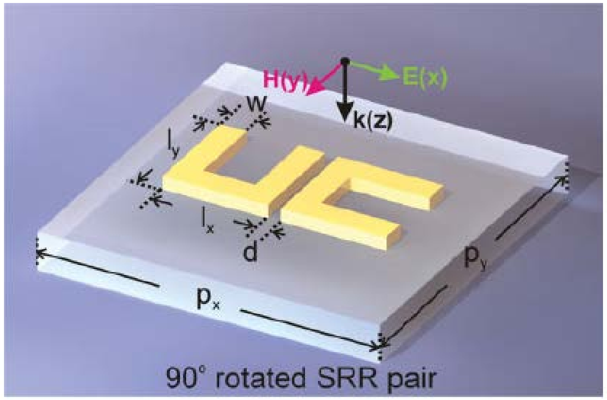


E. Plum, J. Zhou, J. Dong, V. A. Fedotov, T. Koschny, C. M. Soukoulis, and N. I. Zheludev1, Phys. Rev. B **79**, 035407 (2009).

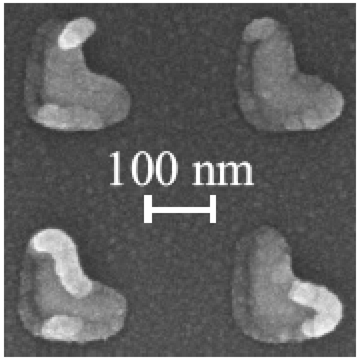
Chiral geometries



W. Zhang, A. Potts and D. M. Bagnall, J. Opt. A **8**, 878-890 (2006).



Na Liu, S. Kaiser and H. Giessen,
Adv. Mater. **20**, 4521–4525 (2008).

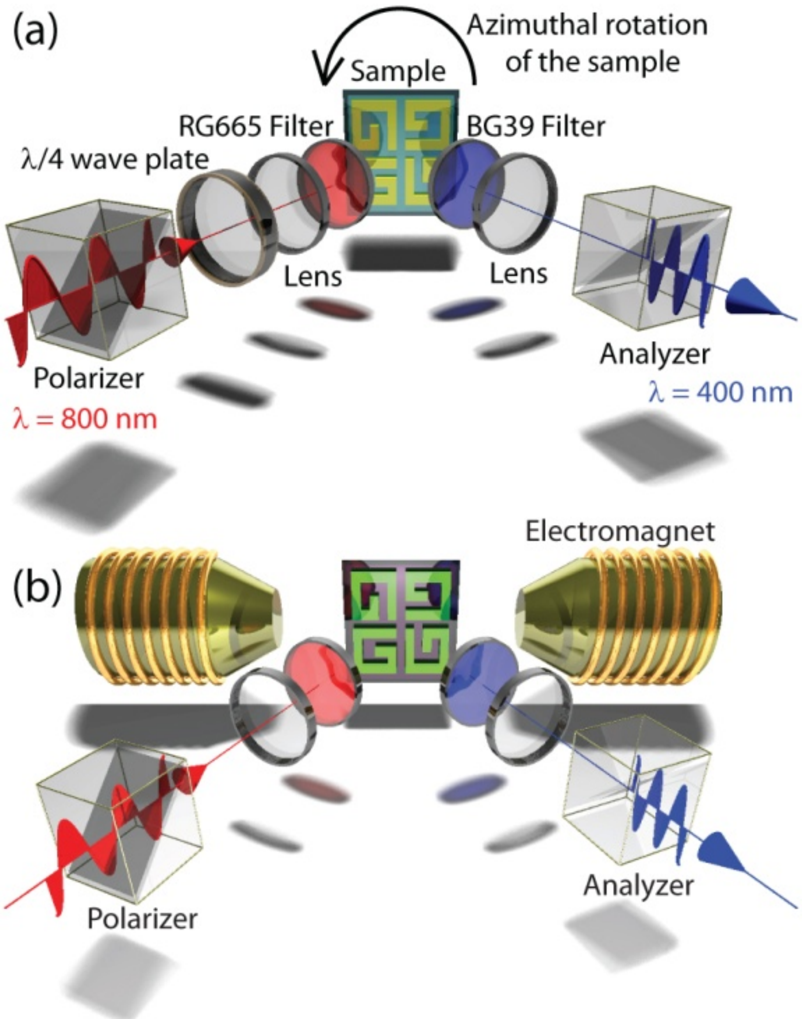


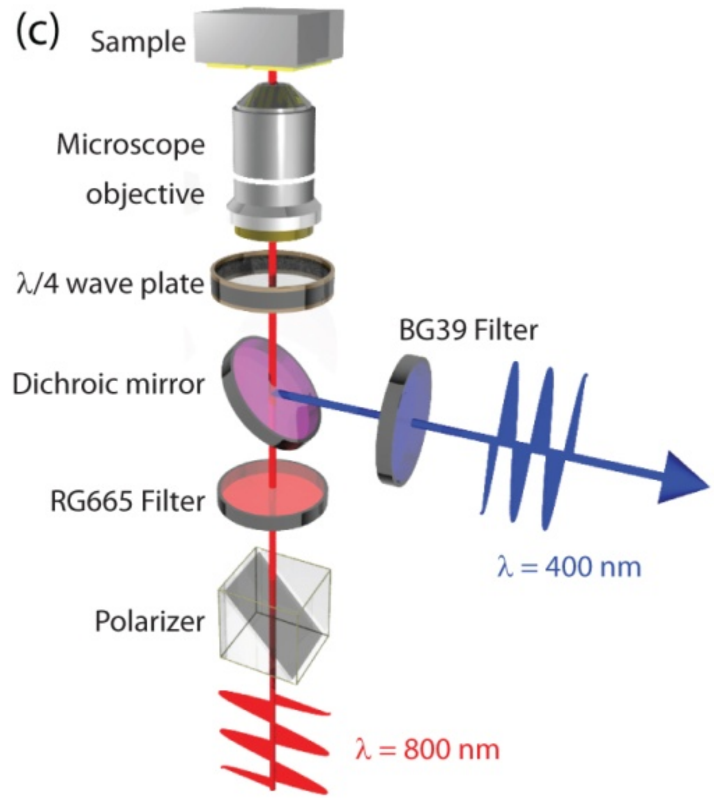
B.K. Canfield, S. Kujala, K. Laiho, K. Jefimovs, J. Turunen, and M. Kauranen, Opt. Express **14**, 950-955 (2006).

There are many interesting aspects of chiral metamaterials.

All of these surfaces can be studied with SHG techniques.

A variety of SHG techniques can be used to study surface symmetries





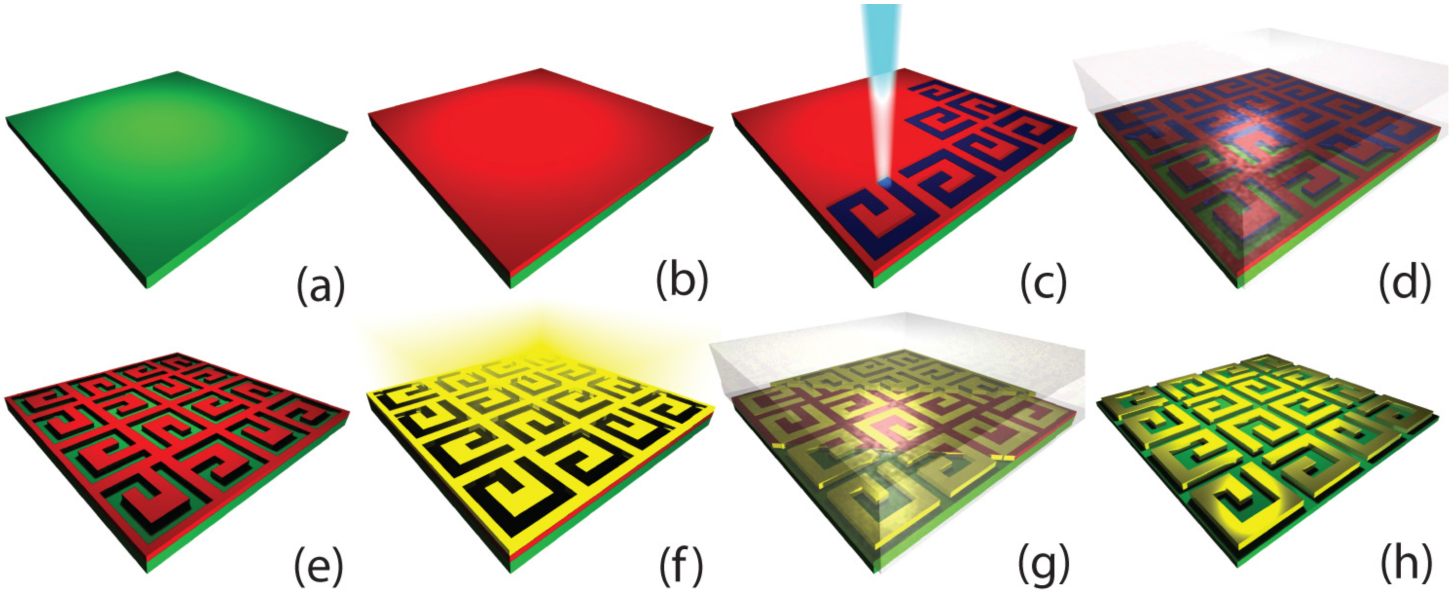
You can manipulate the fields:

$$\mathbf{P}_i(2\omega) = \chi^{(2)}_{ijk} : \mathbf{E}_j(\omega)\mathbf{E}_k(\omega)$$

and manipulate the tensor…

Chiral G-shaped gold nanostructures

With modern nanostructuring techniques, such as Electron Beam Lithography, a surface can be endowed with virtually any possible symmetry.



What is the SHG response from such a surface?

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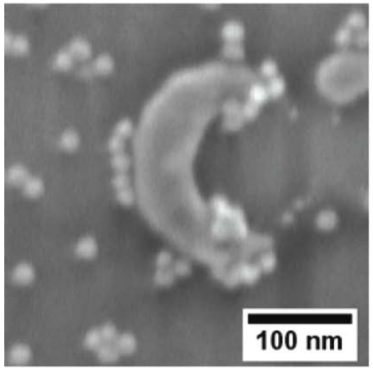
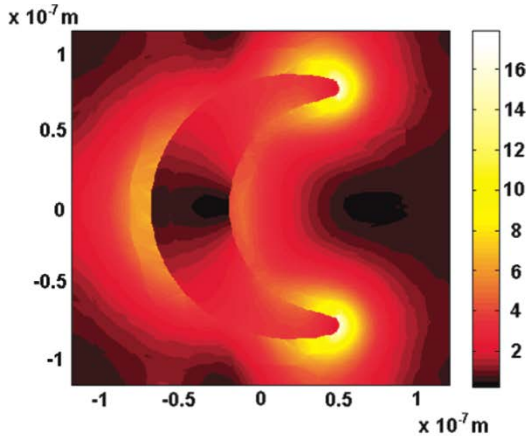
Photochemical reactions, molecular reorientation and enhanced optical properties

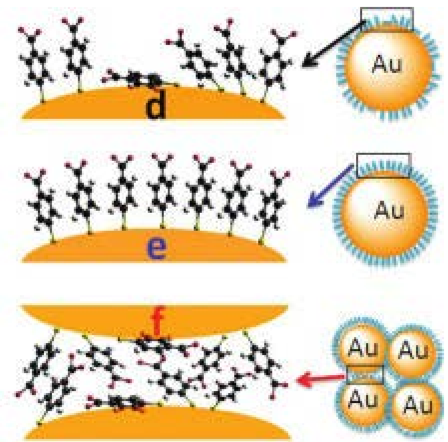




a) SEM image

b) Calculation

K.H. Dostert, M. Álvarez, K. Koynov, A. del Campo, H.J. Butt, and M. Kreiter, "*Near Field Guided Chemical Nanopatterning",* Langmuir 28, 3699-3703 (2012).



Tao Chen, Hong Wang, Gang Chen, Yong Wang, Yuhua Feng, Wei Shan Teo, Tom Wu, and Hongyu Chen, "*Hotspot-Induced Transformation of Surface-Enhanced Raman Scattering Fingerprints",* ACS Nano 4 (6), 3087-3094 (2010).

Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

Shuming Nie* and Steven R. Emory

Abstract: Optical detection and spectroscopy of single molecules and single nanoparticles have been achieved at room temperature with the use of surface-enhanced Raman scattering. Individual silver colloidal nanoparticles were screened from a large heterogeneous population for special size-dependent properties and were then used to amplify the spectroscopic signatures of adsorbed molecules. For single rhodamine 6G molecules adsorbed on the selected nanoparticles, the intrinsic Raman enhancement factors were on the order of 10^{14} to 10^{15}, much larger than the ensemble-averaged values derived from conventional measurements. This enormous enhancement leads to vibrational Raman signals that are more intense and more stable than single-molecule fluorescence.

Science 275, 1102 (1997).

Studying near-field enhancements can benefit from a surface-specific optical technique.

Present Collaborators:

Prof. T. Verbiest, *Molecular Electronics and Photonics, INPAC, Dept. of Chemistry, K. U. Leuven, Belgium*

Prof. A. V. Silhanek and Prof. V.V. Moshchalkov, *Nanoscale Superconductivity and Magnetism & Pulsed Fields, Dept. of Physics and Astronomy, INPAC, K. U. Leuven, Belgium*

E. Osley and Dr. Paul Warburton, *London Centre for Nanotechnology, University College London, UK*

B. De Clercq, Prof. M. Ameloot,
Dept. of Physiology, University Hasselt, Belgium

C. Biris, Dr. N. C. Panoiu,
Dept. of Electronic & Electrical Engineering, University College London, UK

X. Zheng, Dr. V. Volskiy, Prof. G.A.E. Vandenbosch, *ESAT-TELEMIC, Dept. of Electrical Engineering, K. U. Leuven, Belgium*

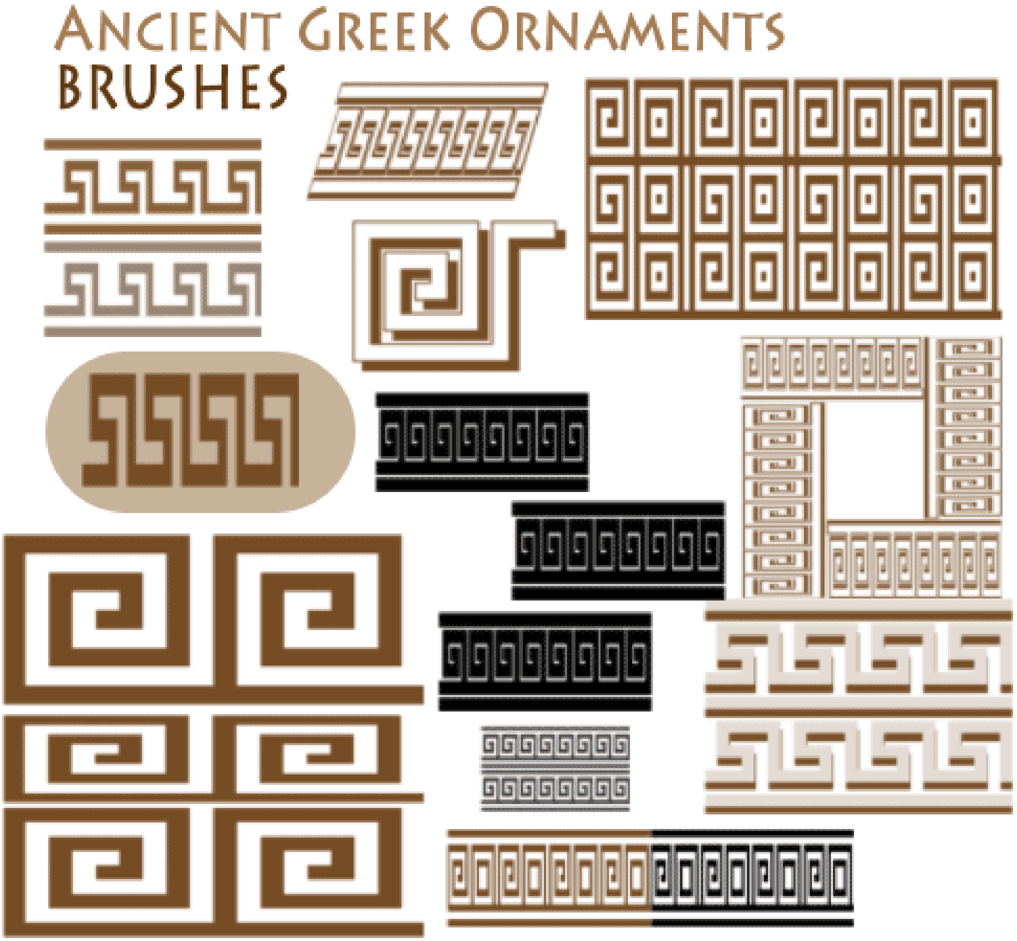
Prof. O. A. Aktsipetrov, *Laboratory of Nonlinear Optics Dept. of Physics, Moscow State University, Russia*

Dr. D. Slavov, Prof. S. Cartaleva,
Institute for Electronics, Bulgarian Accademy of Sciences, Bulgaria

Dr. G. Tsutsumanova, Prof. S. Russev,
Dept. of Solid State Physics, Sofia University, Bulgaria

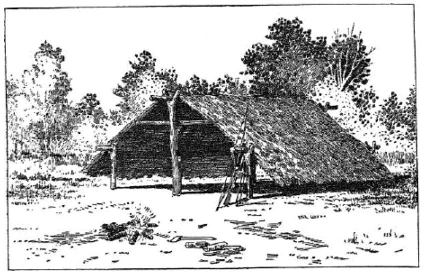
Dr. A. Kuznetsov, Dr. C. Reinhardt, Prof. B. Chichkov,
Laser Zentrum Hanover, Hanover, Germany

The Ancient Greeks greatly appreciated square spirals



But they were not the only ones!

In Ancient Egypt



The Ancient Egyptian hieroglyph for the sound "h".

The Ancient Italians

A Latial hut-urn decorated with white paint.

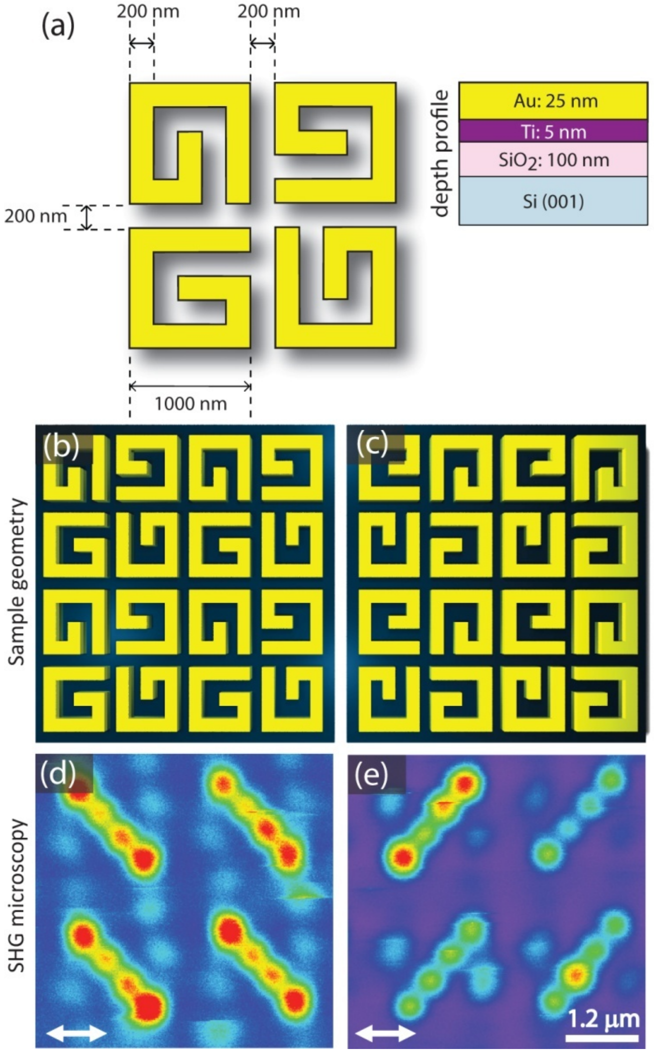
Dated in the Early Iron Age, between 10th and 6th century, before the Common Era.

Situated in the *Museo Nazionale Romano: Terme di Diocleziano*, on the first floor.

Overview

1. Introduction
2. The importance of symmetry
3. The importance of local field enhancements
   a) Linearly polarized light
   b) Circularly polarized light
4. The road ahead
5. Summary

Scanning second harmonic generation microscopy reveals a pattern of hotspots



Rather than showing a G-shaped signal, the SHG microscopy reveals a pattern of clearly defined hotspots.

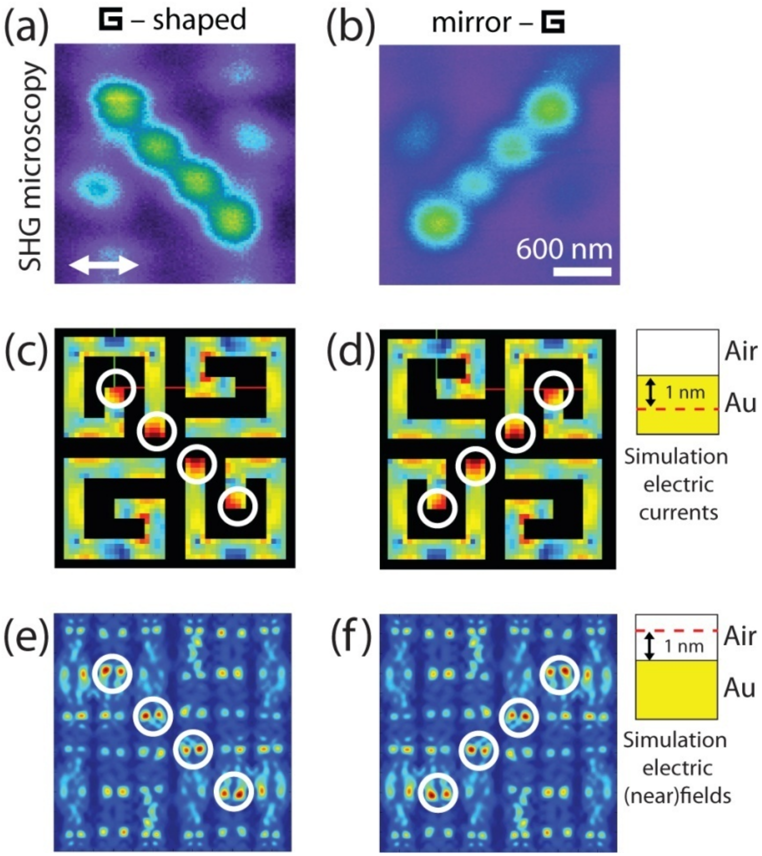
The white arrows indicate the direction of the linear polarization.

The color coded intensities increase from purple, through green, then yellow to red.

Ti was used as adhesion layer.

Are these hotspots SHG-specific?

The second harmonic hotspots match numerical simulations at the first harmonic



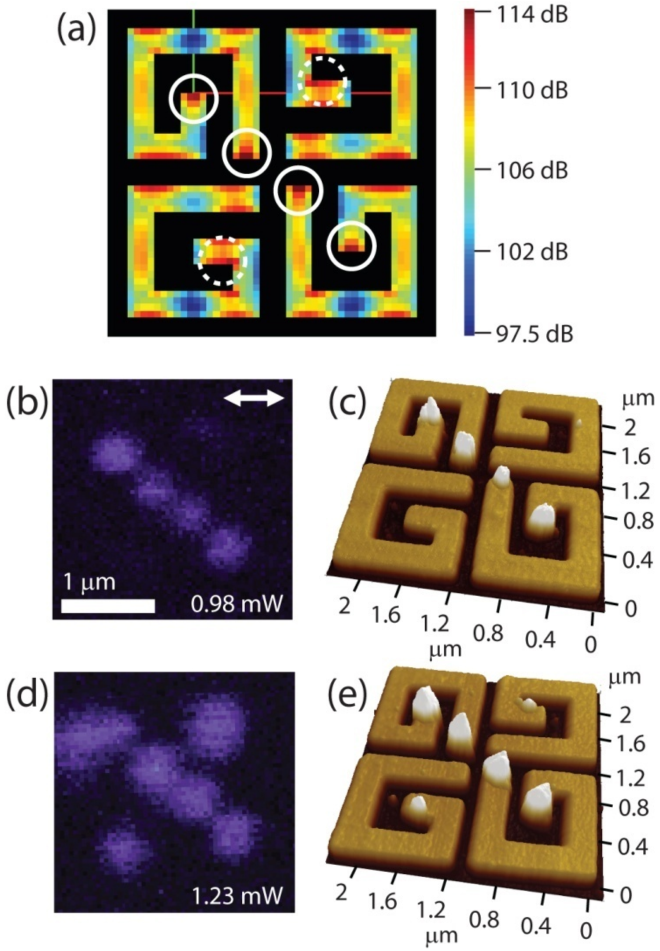
The pattern of experimentally recorded second harmonic hotspots matches the pattern of numerically simulated local field enhancements at the fundamental frequency.

Simulations of the electric current were performed with MAGMAS – an in-house Maxwell equations solver.

Simulations of the electric near-fields were performed with RSoft's Diffract MOD.

Can we find experimental evidence for the location of the near-field enhancements?

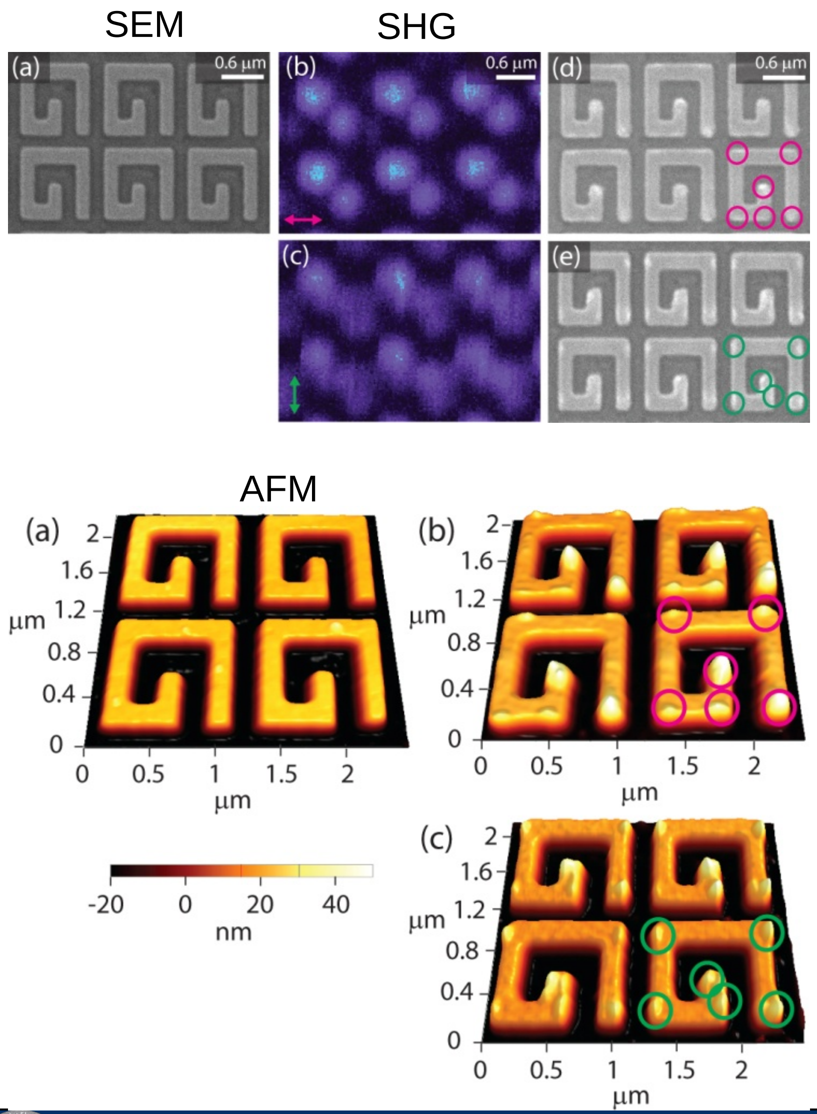
Experimental mapping of the near-field matches the SHG hotspots

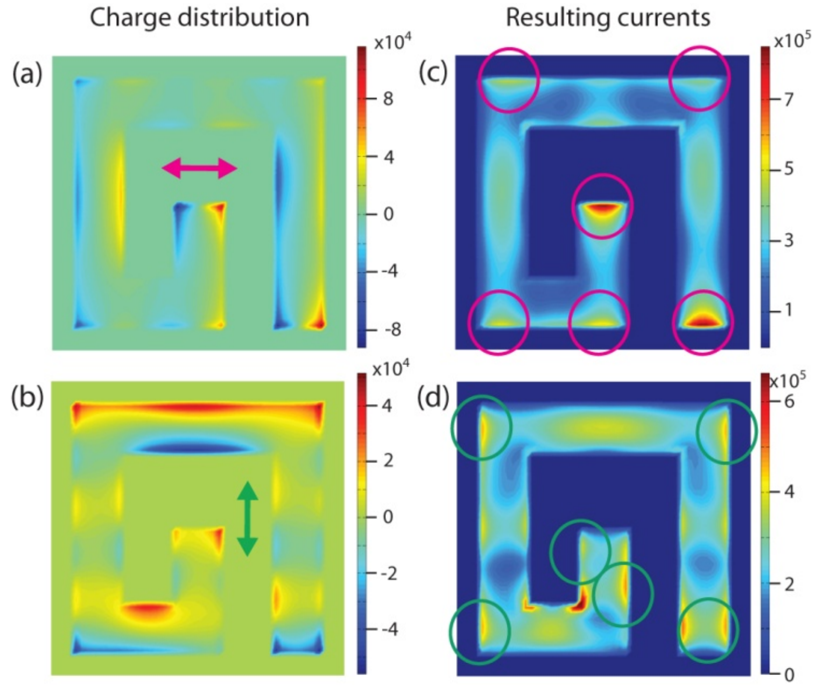


In Ni G-shaped nanostructures, we have observed that nanobumps can appear at the surface of the nanostructures, precisely in the locations of the calculated near-field. The pattern of these nanobumps matches the pattern of SHG hotspots and the numerical simulations.

Are these imprints polarization dependent?

The imprints are dependent on the polarization direction

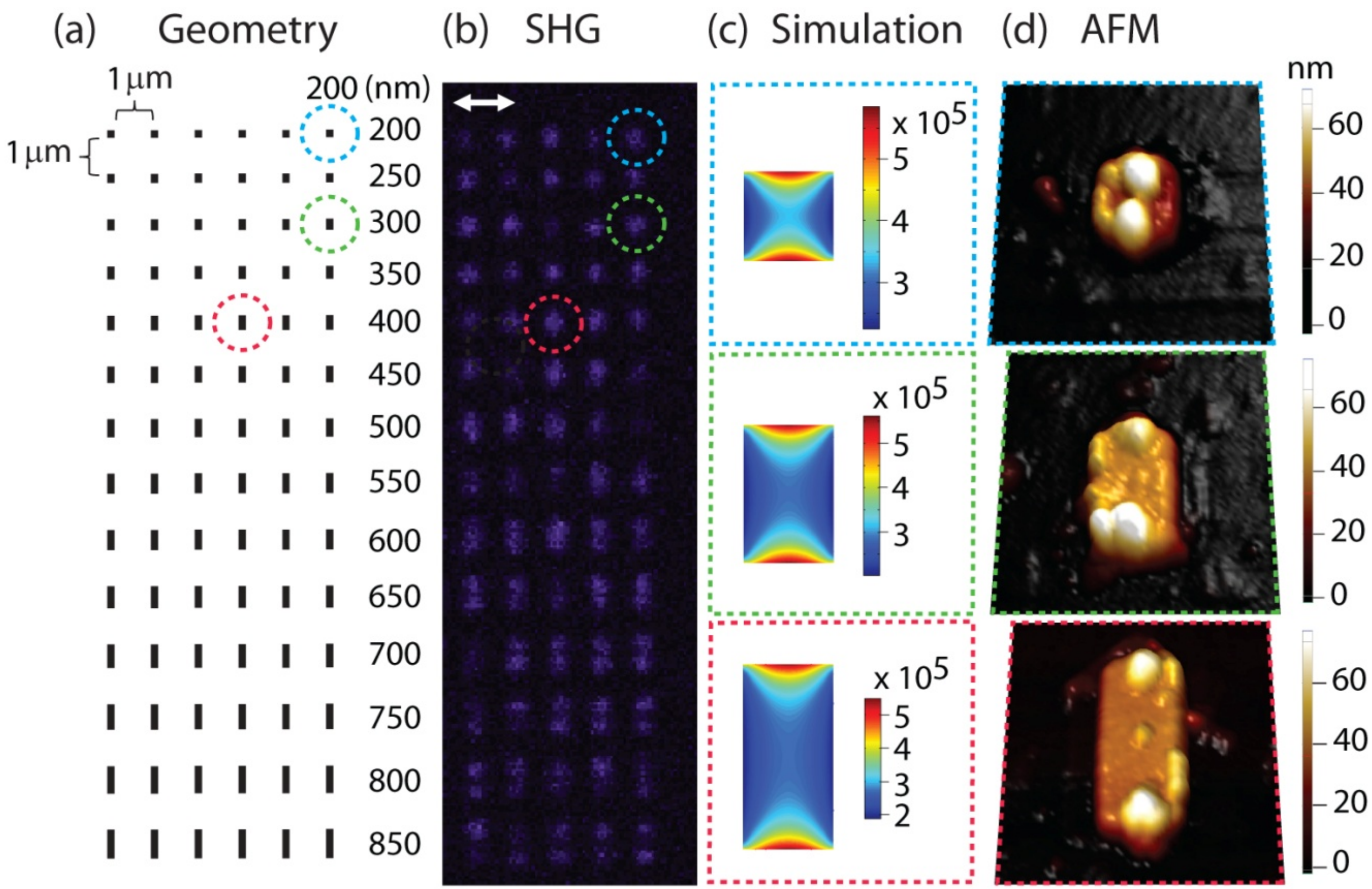




Although rearranged, there nanostructures are still G-shaped.

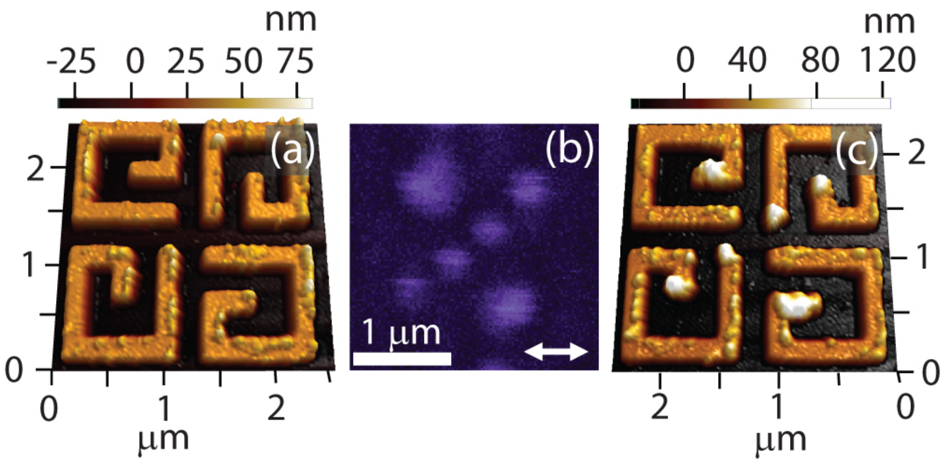
What about other geometries?

Sub-wavelength nanobumps

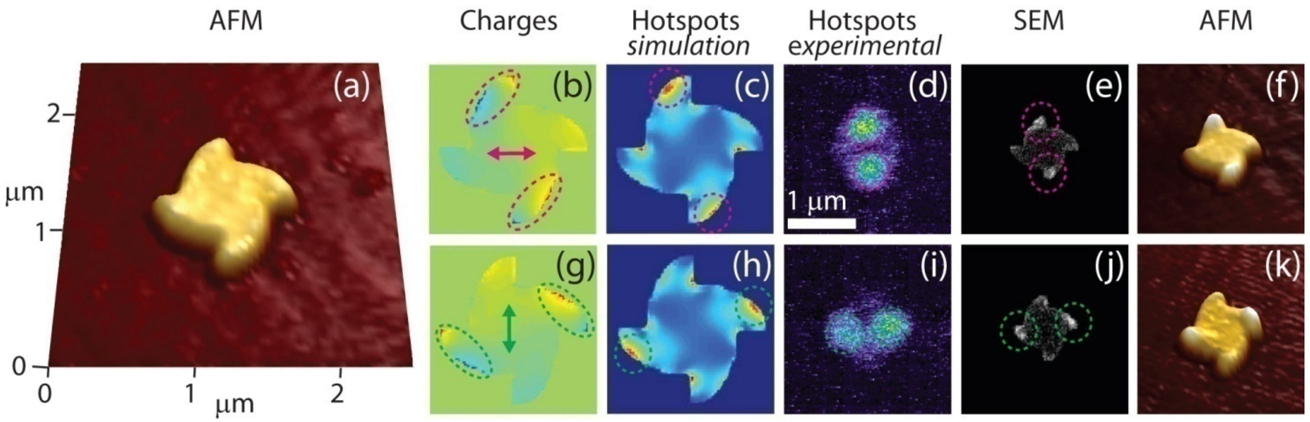


What about other materials?

Imprinting also occurs in gold and palladium



Palladium can also be imprinted;



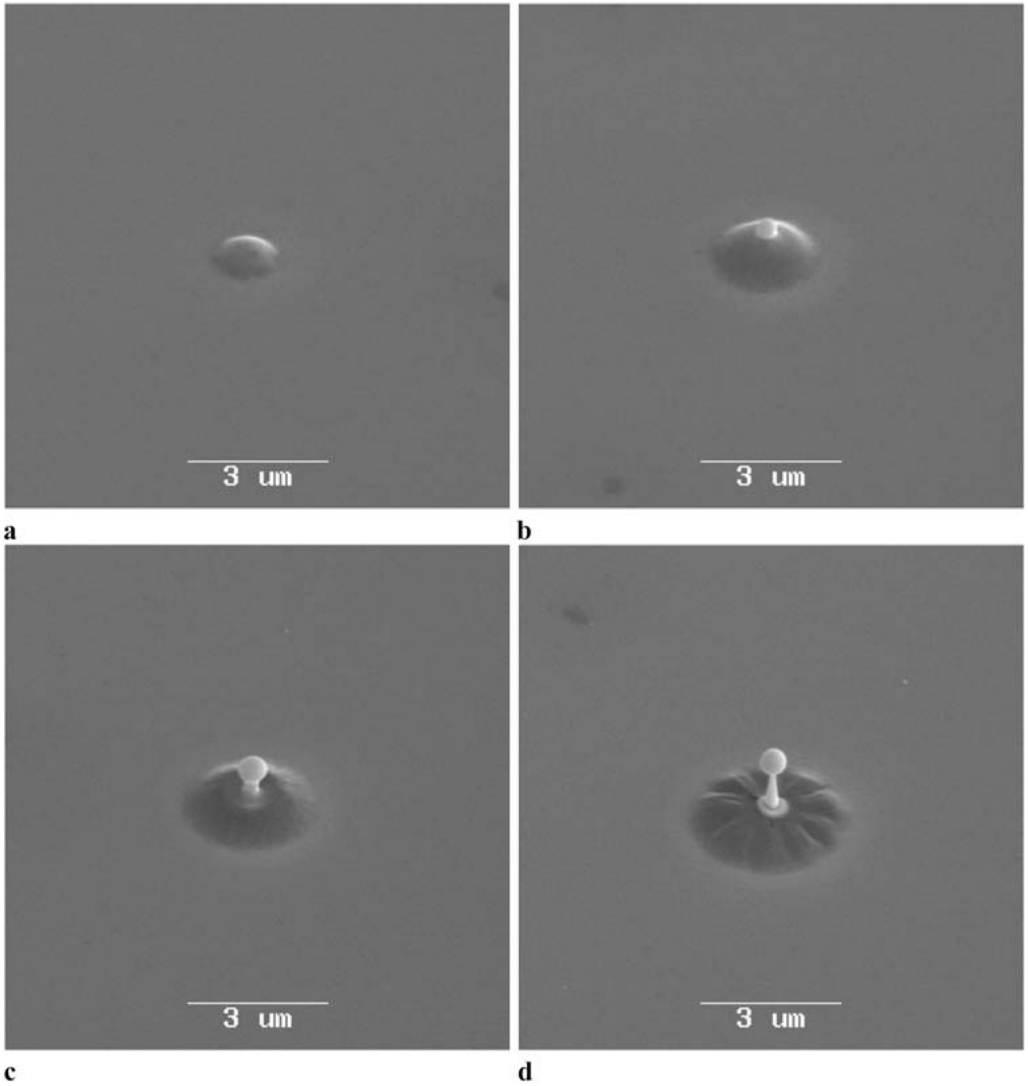
In star-shaped gold nanostructures, the locations of SHG hotspots, calculated near-field enhancements and nanobumps all match.

What is the physical mechanism causing the nanobumps?
How can we get material moving **upwards**?

Water back-jets project material "upwards"

Could the nanobumps be caused by a similar mechanism?

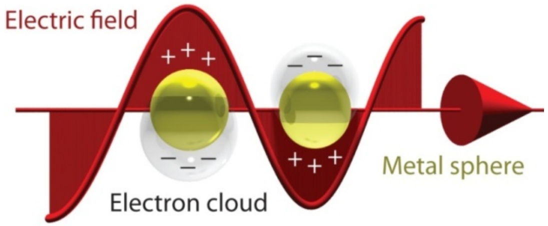
Nanojets from a continuous gold film



A single femtosecond light pulse can locally melt the surface of gold and trigger hydrodynamic processes. It is possible to follow these processes step-by-step by varying the pulse power.

The hydrodynamic process seem to require a large amount of material.

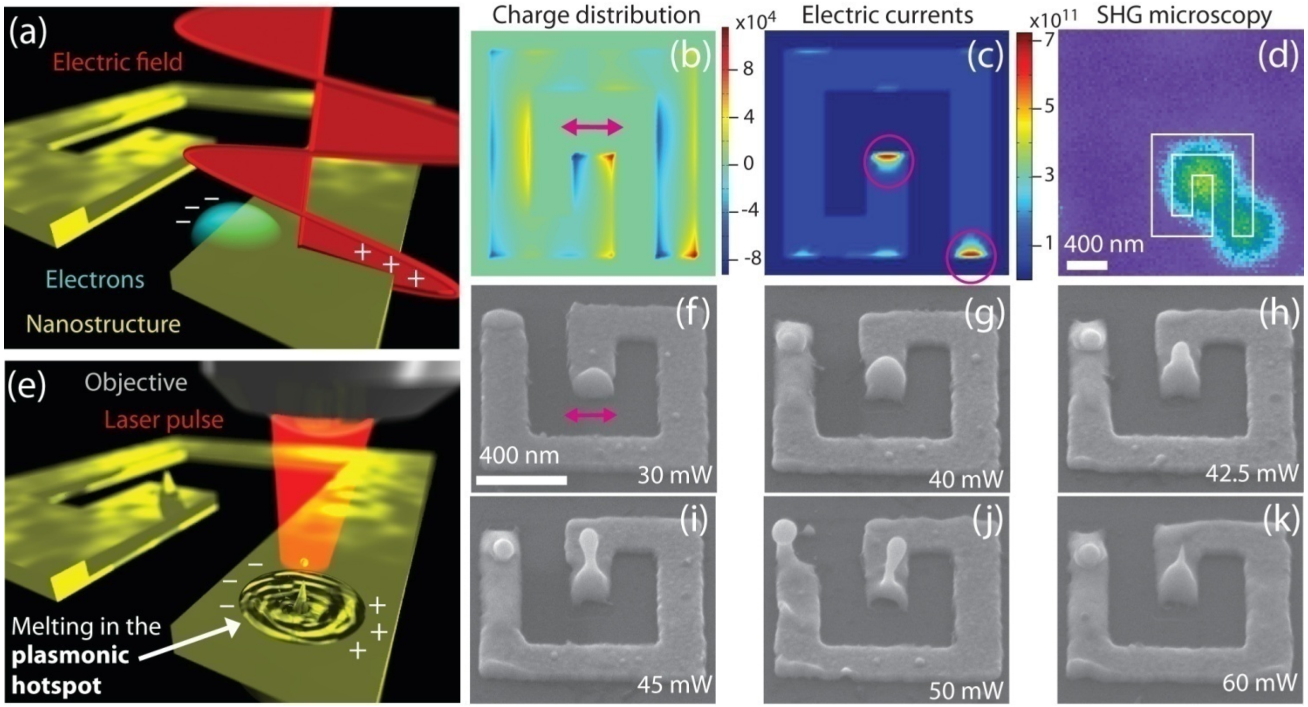
What is the link with plasmons?



A.I. Kuznetsov, *et al.*, "*Nanostructuring of thin gold films by femtosecond lasers*", Appl Phys A **94**, 221–230 (2009) .

Nanojets from G-shaped gold nanostructures

We used single femtosecond light pulses at the wavelength of 800 nm. The illumination area on the sample surface was a square with side length of 6 μm.



What about circularly polarized light

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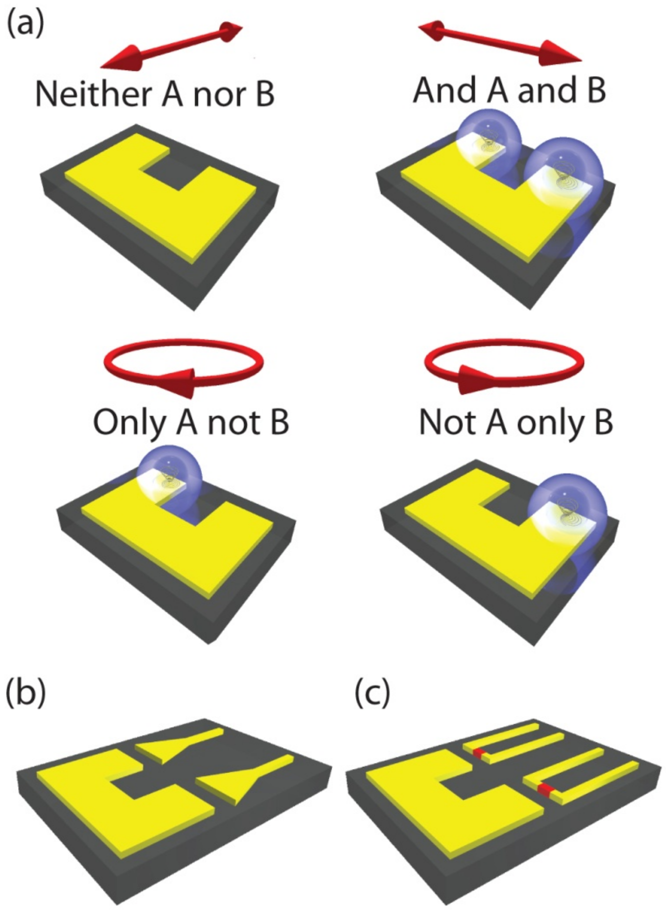
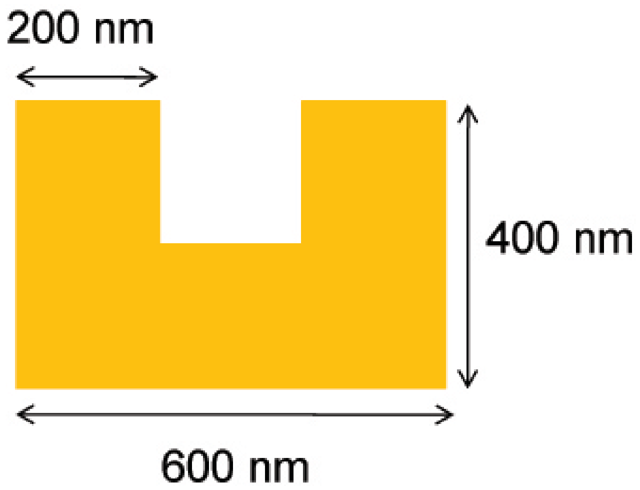
U-shaped nano-switches schematic diagram

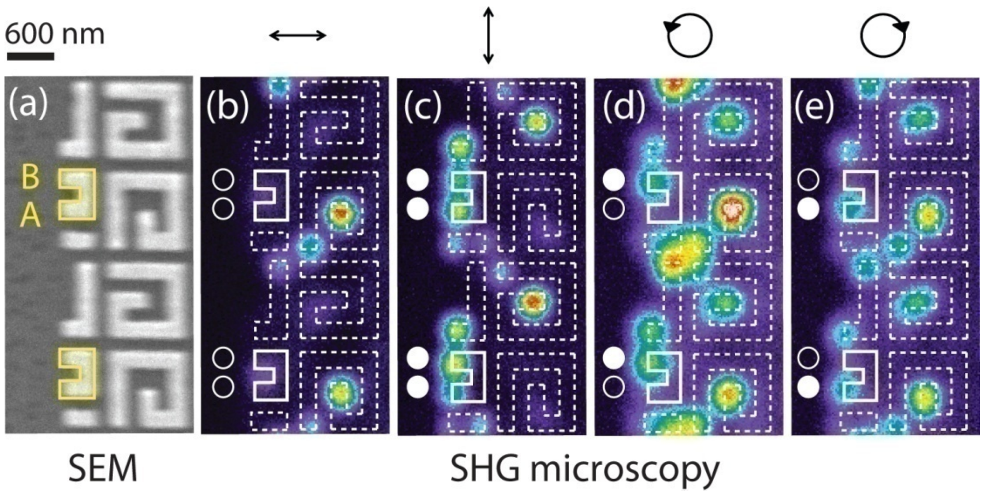


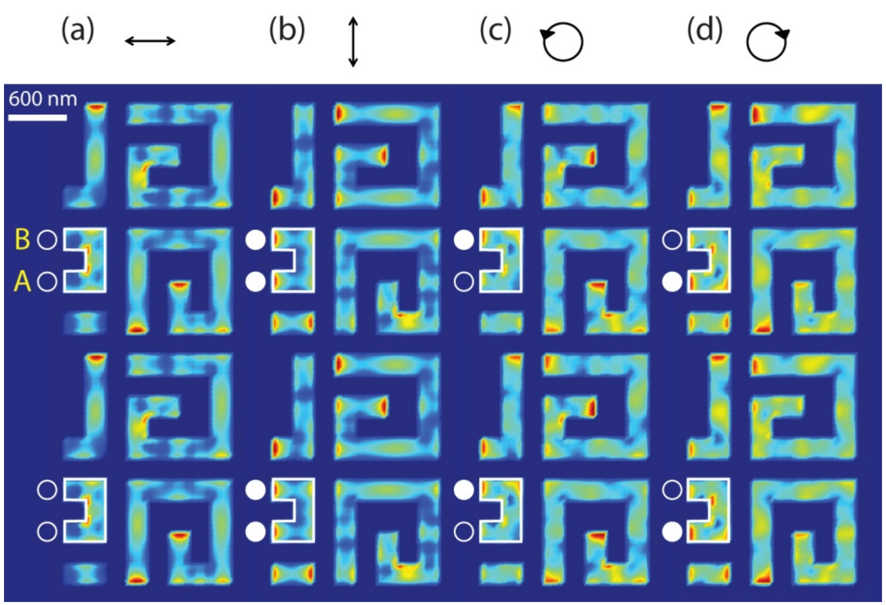
Depending on the polarization state of the incoming light, the two branches (outputs A and B) of a golden U-shaped nanostructure, give rise to localized SHG sources, or **hotspots**, that are due to local field enhancements.



V. K. Valev, *et al.*, "*U-shaped switches for optical information processing at the* nanoscale", Small **7**, 2573 (2011).

U-shaped nano-switches SHG data



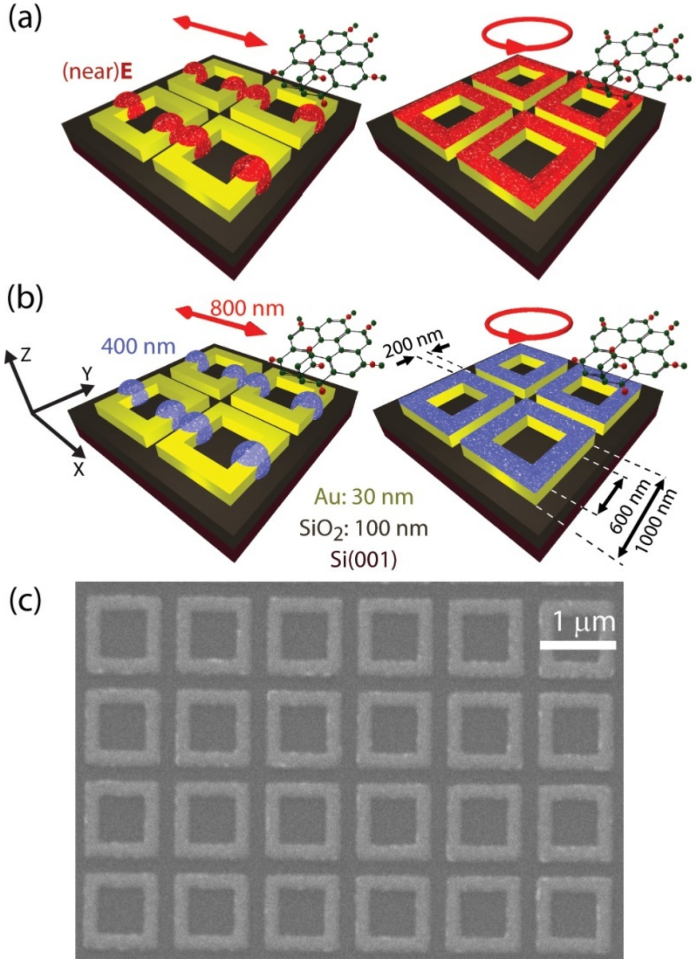


The color-coded intensities increase from purple through blue, green, yellow and red to white.

The locations of the SHG hotspots are displayed by superposing them on the SEM micrographs. For clarity, the presence or absence of hotspots on the U-shaped nanostructures is indicated by full or empty white circles, respectively.

What if we closed the U geometry, forming a ring?

Square-rings for distributing the optical near-field on the sample surface

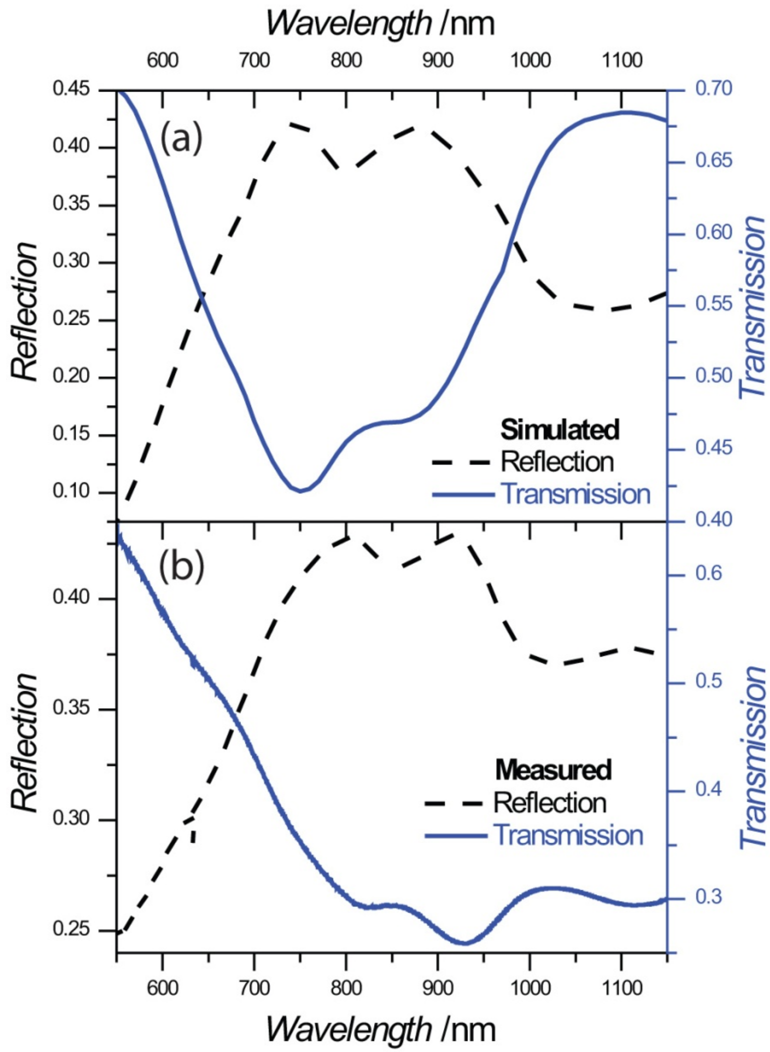


By definition, hotspots are highly localized and, for intense illumination, they can become too hot.

Upon illuminating square-ring-shaped nanostructures with circularly polarized light, the optical near-field can be distributed over the entire sample surface, thereby increasing the useful area and allowing the use of higher illumination intensities

Is there really a resonance to speak about?

Square-rings for distributing the optical near-field on the sample surface



For linearly polarized incident light, reflection and transmission spectra from the square-shaped gold nanostructures were numerically simulated and experimentally measured as is it shown in (a) and (b), respectively.

There is a clear resonance around 800 nm, which corresponds to our wavelength of excitation.

We can now examine the optical near-field by means of numerical simulations.

V. K. Valev, *et al.*, "*Distributing the optical near field for efficient field-enhancements in nanostructures*", Adv. Mater. (2012), in press.

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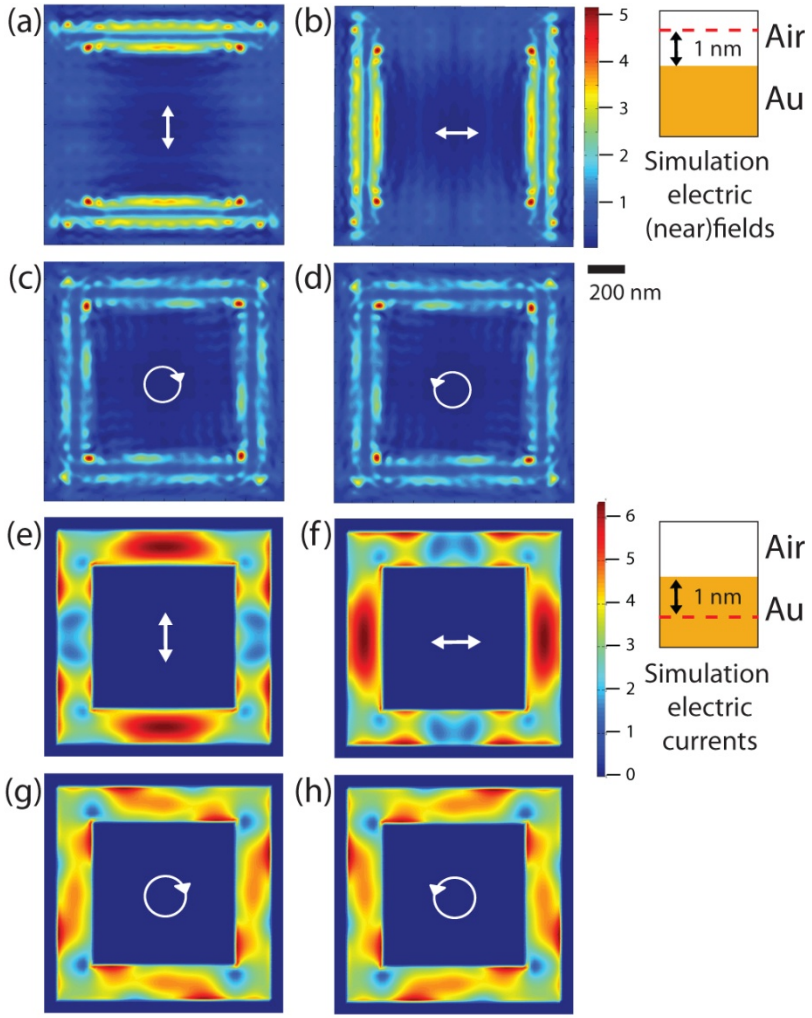
LEUVEN

Numerical simulations of the optical near-field



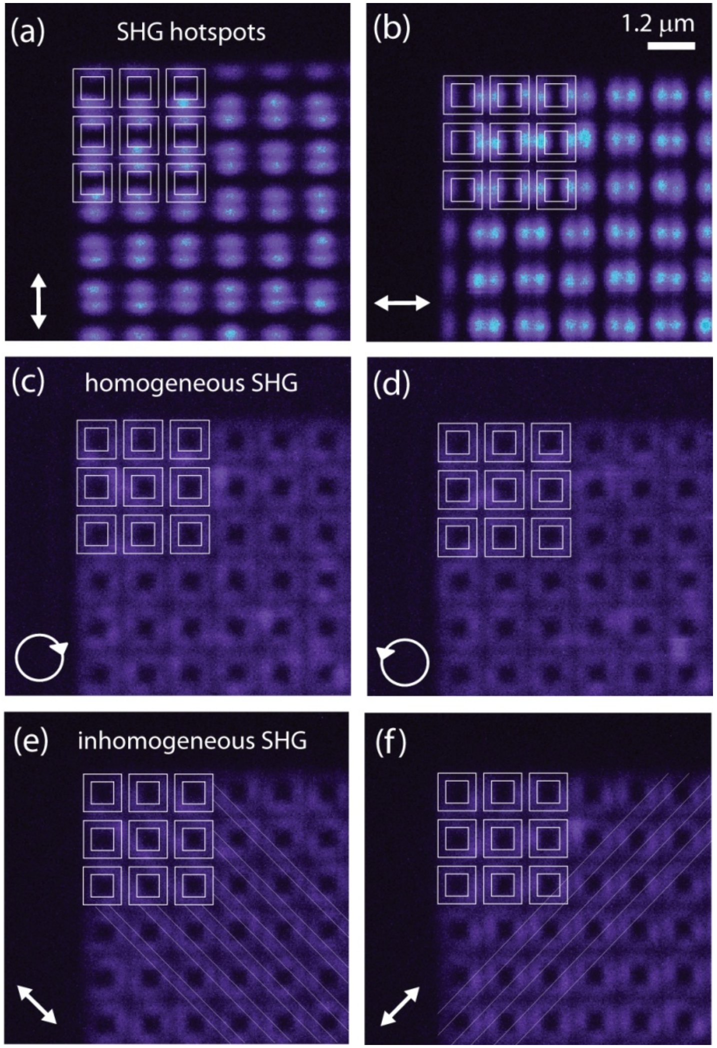
For linearly polarized light, the near-field is **concentrated** on the sides perpendicular to the direction of linear polarization.

For circularly polarized light, the near-field distribution is more **homogeneous**.

There is a difference in the patterns for left- and right-hand circularly polarized light, indicating that the **chirality of light** has been **imparted** on the **charge distribution**.

What about experimental data?

Second harmonic generation confirms the simulation results



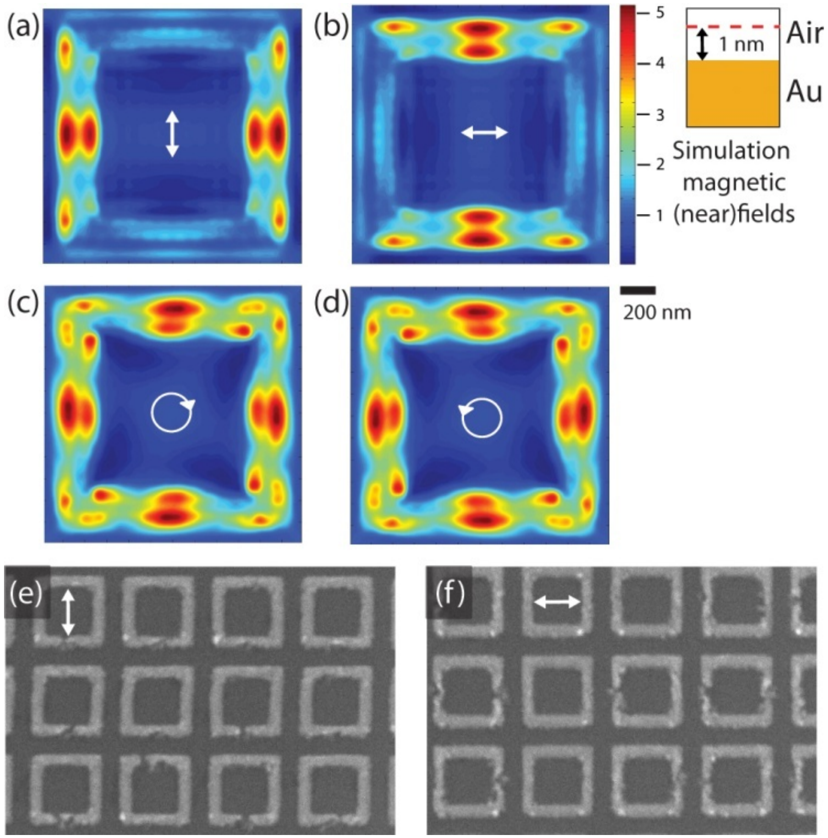
For linearly polarized light, the near-field is **concentrated** on the sides perpendicular to the direction of linear polarization.

For circularly polarized light, the near-field distribution is more **homogeneous**.

For linearly polarized light along 45°, the SHG signal is not homogeneous, indicating that the homogeneity of the signal **requires** circularly polarized light.

Is this SHG pattern really related to the electric field? How reliable is the location of the SHG hotspots?

Location and origin of the SHG hotspots



For linearly polarized light, the magnetic near-field is concentrated on the sides **parallel** to the direction of linear polarization.

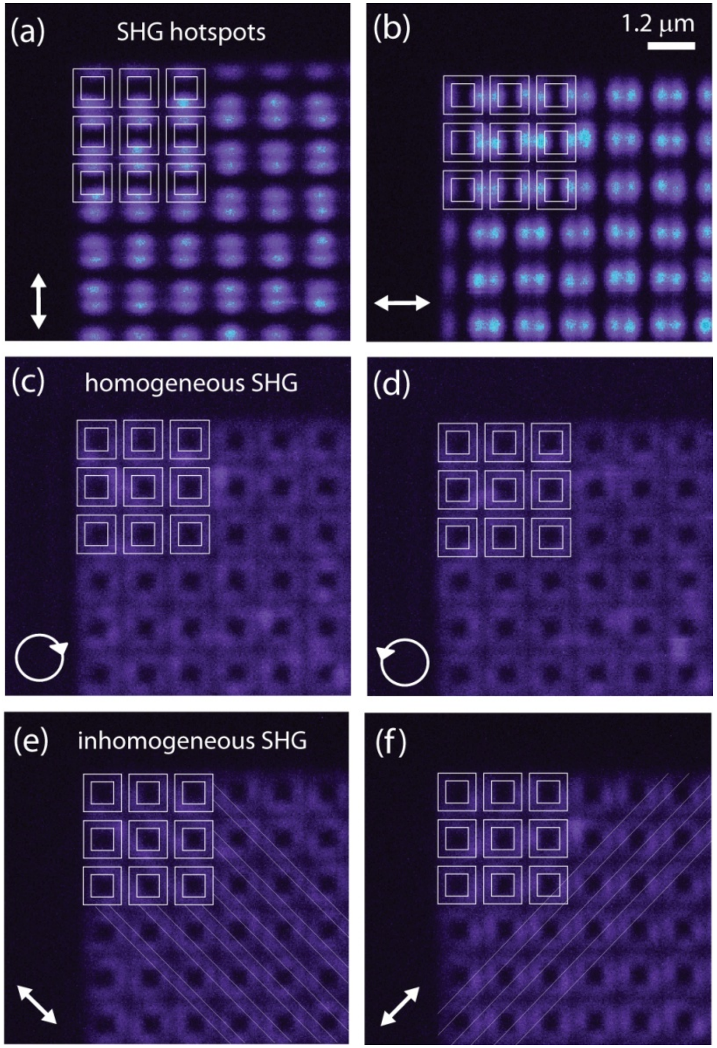
For circularly polarized light, the magnetic near-field distribution is not more homogeneous but instead presents **four hotspots** – one on each side of the square.

For linearly polarized light, sub-wavelength plasmon-assisted laser-ablation shows that the hotspots are situated on the sides **perpendicular** to the direction of linear polarization.

How about randomly oriented linearly polarized light?

V. K. Valev, *et al.*, "*Distributing the optical near field for efficient field-enhancements in nanostructures*", Adv. Mater. (2012), in press.

What about "randomly polarized" light?



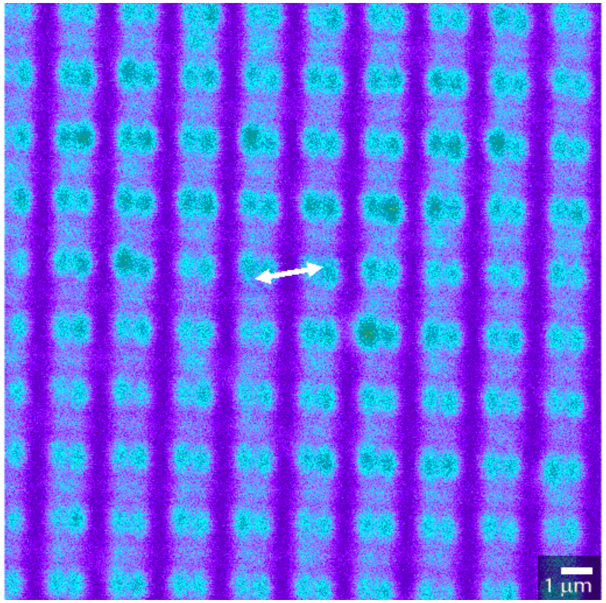
For linearly polarized light, the near-field is **concentrated** on the sides perpendicular to the direction of linear polarization.

For circularly polarized light, the near-field distribution is more **homogeneous**.

For linearly polarized light along 45°, the SHG signal is not homogeneous, indicating that the homogeneity of the signal **requires** circularly polarized light.

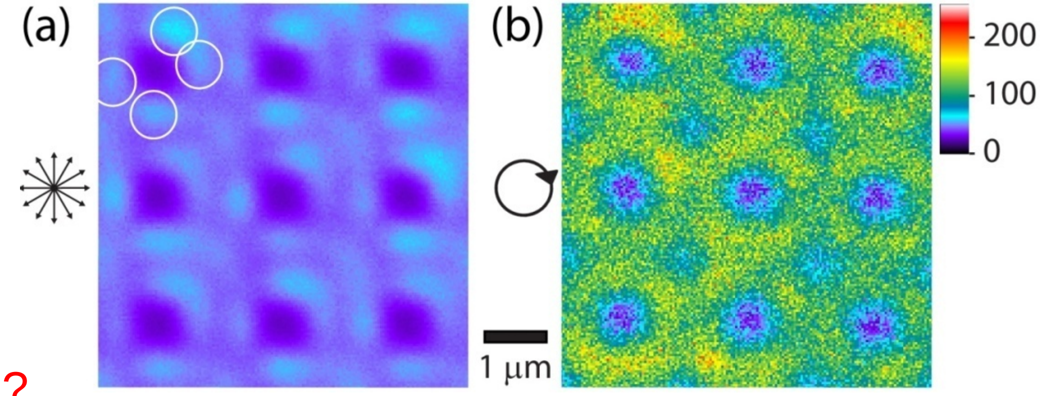
If the pattern of hotspots follows the direction of linearly polarized light then, for randomly oriented linearly polarized light, the near-field should also be homogeneous.

Randomly oriented linearly polarized light yields inhomogeneous near-field enhancement



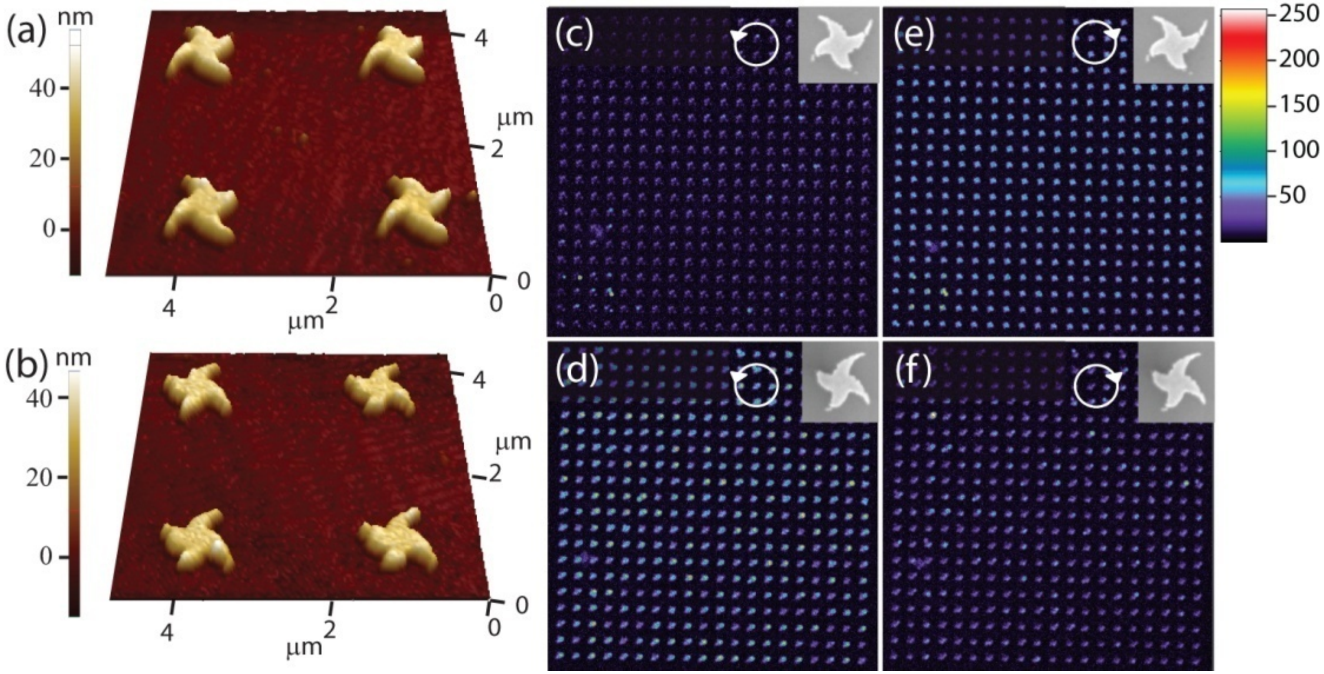
Upon rotating the direction of linearly polarized light, the pattern of hotspots does not follow. Instead, the hotspots appear to be “pinned” by the strong coupling between nanostructures along the X and Y directions.

The average signal is clearly inhomogeneous. There is some drift of the sample stage.



How about using chiral nanostructures?

Chiral nanostructured metal surfaces with decoupled nanoelements



Towards a metamolecular surface: individual nanostructures confer their chiral second harmonic properties to an entire surface. A clear SHG-CD effect is visible from every individual nanostructure.

On to microscopic surface properties…

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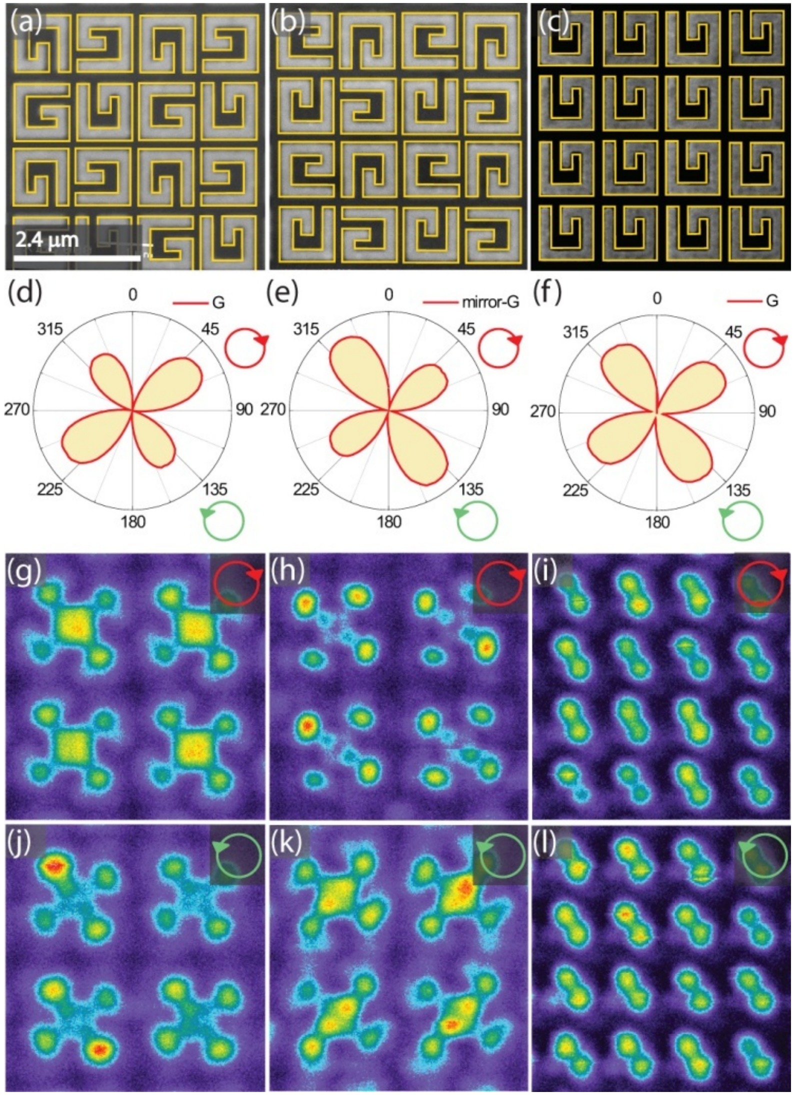
Switching SHG - circular dichroism (CD) by rearranging chiral structures

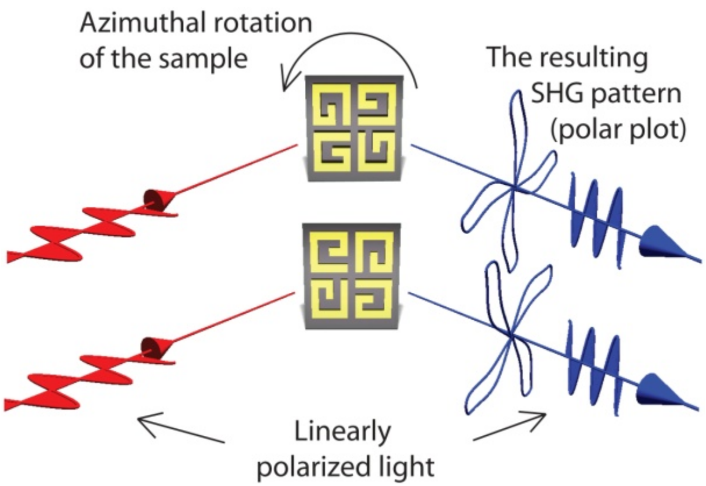


SHG intensity (arb. units) vs. varying ellipticity of the incoming light, i.e. λ/4 wave plate rotation (deg.)

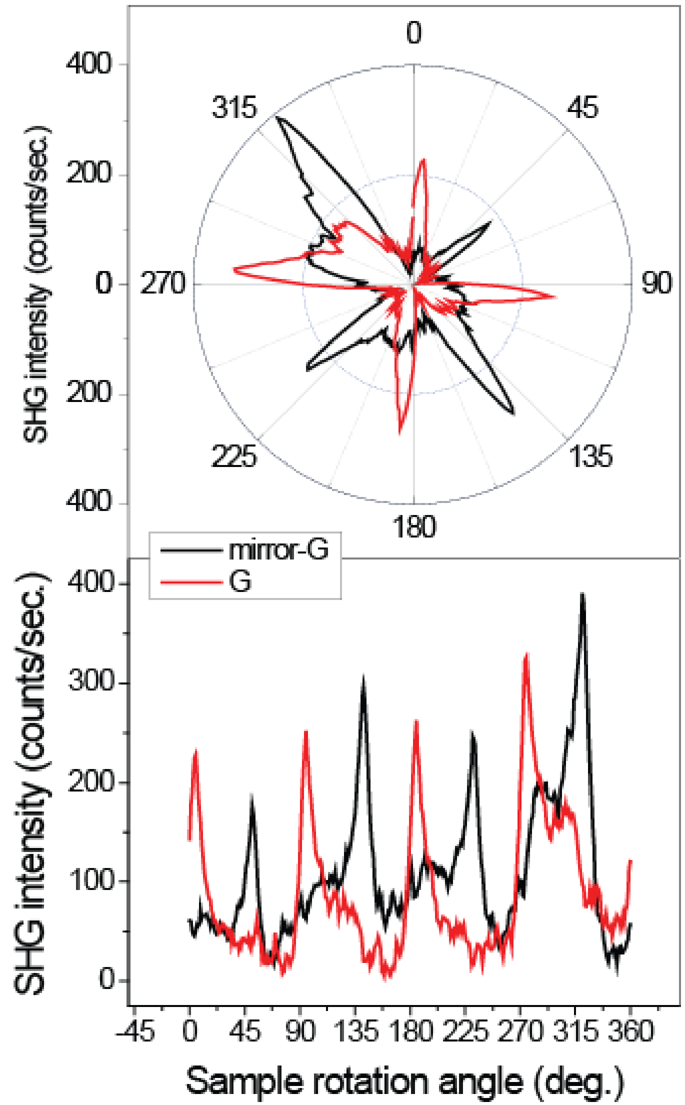
SHG microscopy reveals that the SHG-CD effect is due to supra-structural behavior.

V. K. Valev, *et al*. *“Plasmonic Ratchet Wheels: Switching Circular Dichroism by Arranging Chiral Nanostructures”*, Nano Lett. **9**, 3945 (2009).

Asymmetric Second Harmonic Generation reveals the chirality

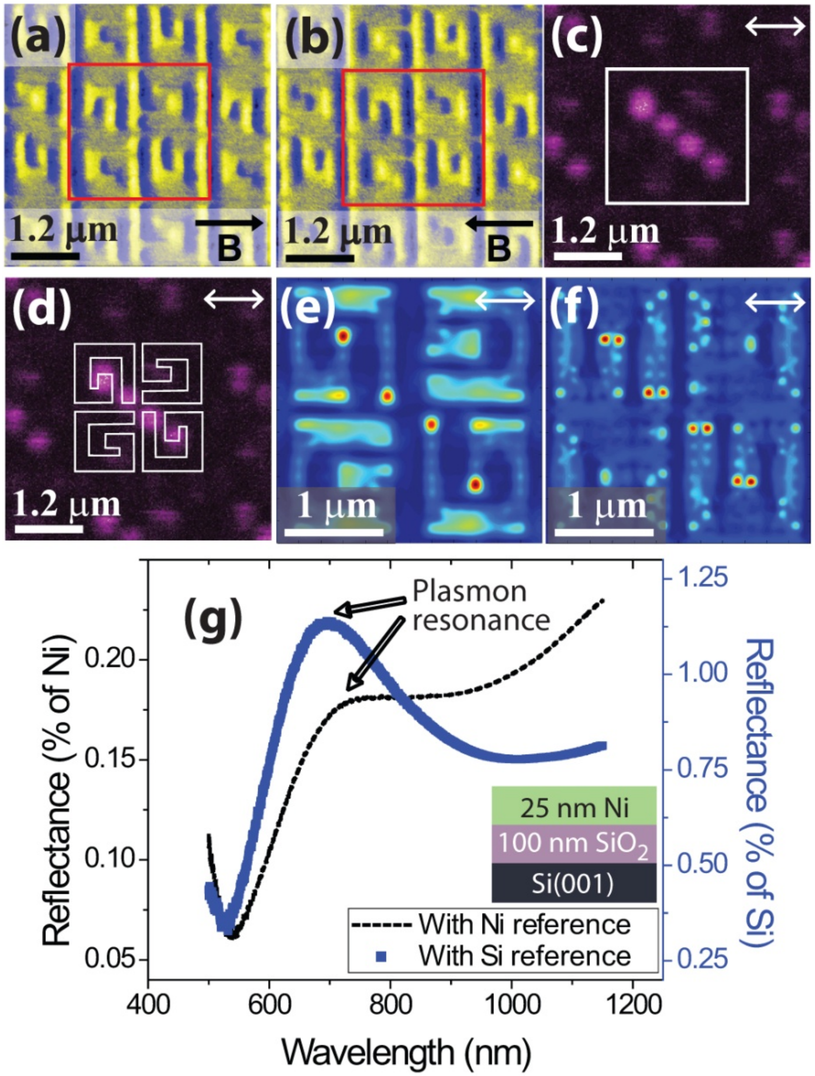


Polarizer along the horizontal (P) direction and analyzer along the vertical (S) direction



Upon azimuthal rotation of the sample, for linearly polarized light, the resulting SHG pattern exhibits a different sense of rotation and a different intensity depending on the handedness.

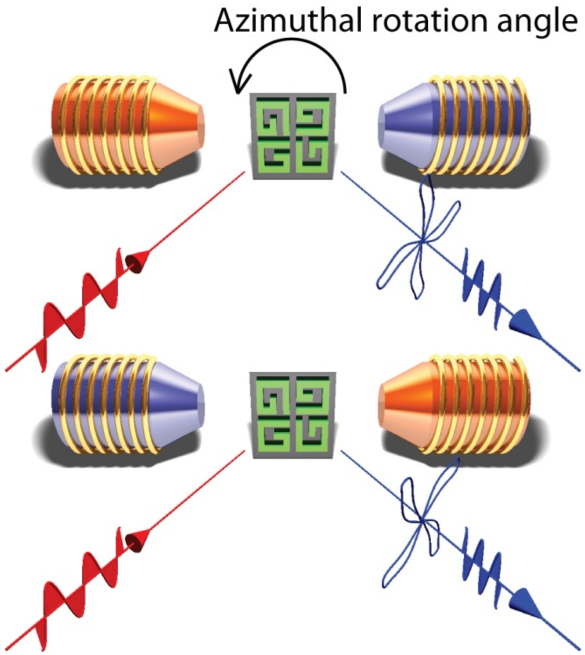
Both plasmons and magnetization are present in Ni G-shaped nanostructures

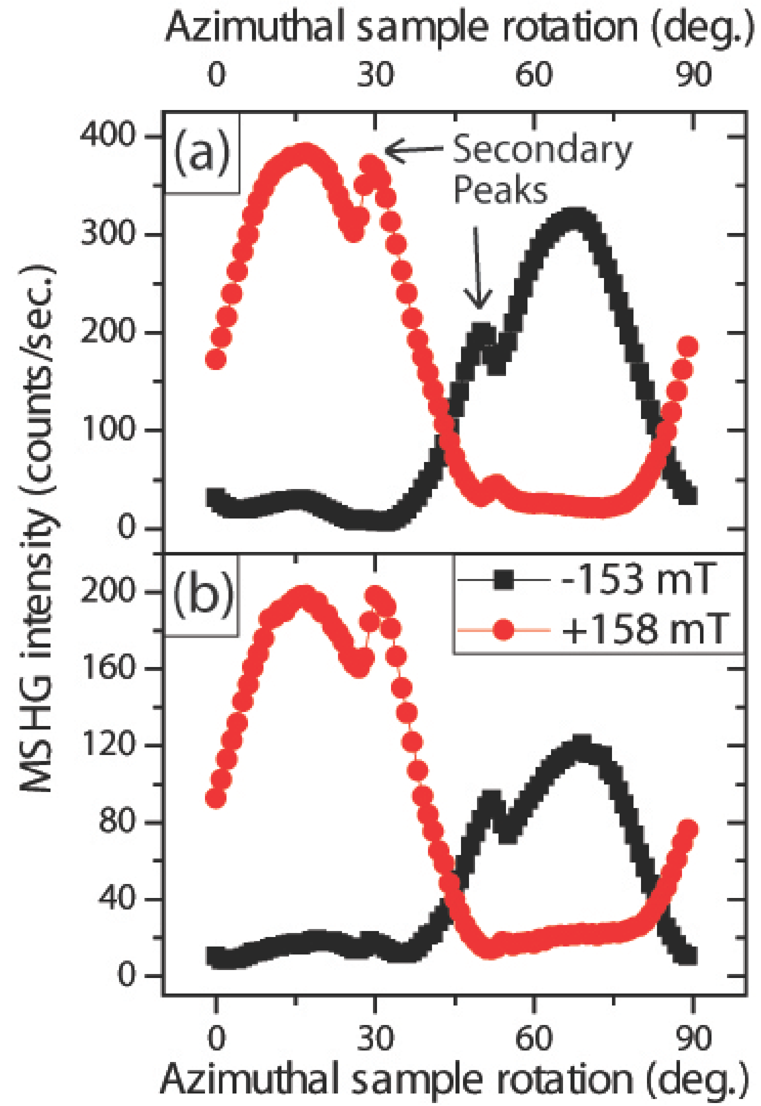


Magnetic force microscopy: the yellow-blue contrast reveals typical in-plane magnetization for B=+25 mT and B=-25 mT, respectively.

The spectra, the SHG micrographs and the simulations indicate the presence of plasmons in the G-shaped nickel nanostructures.

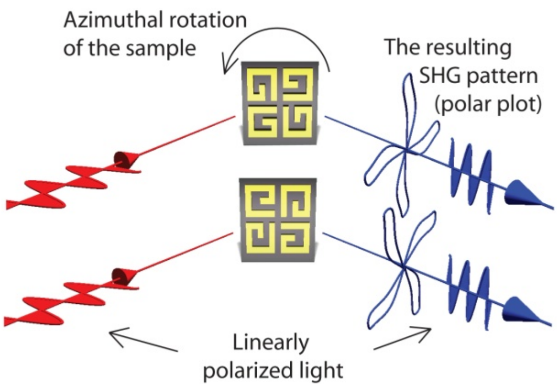
ASHG reveals the direction of magnetization

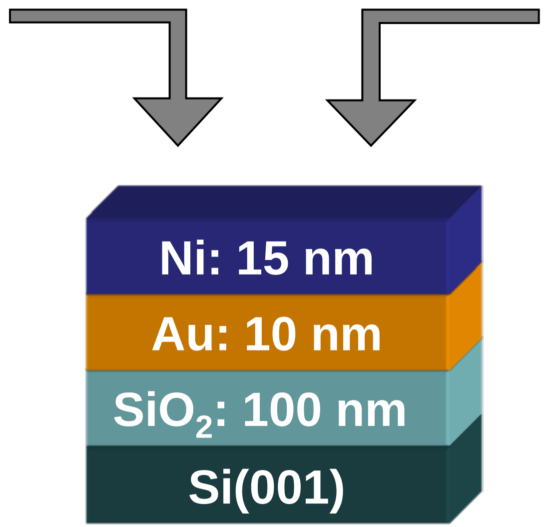


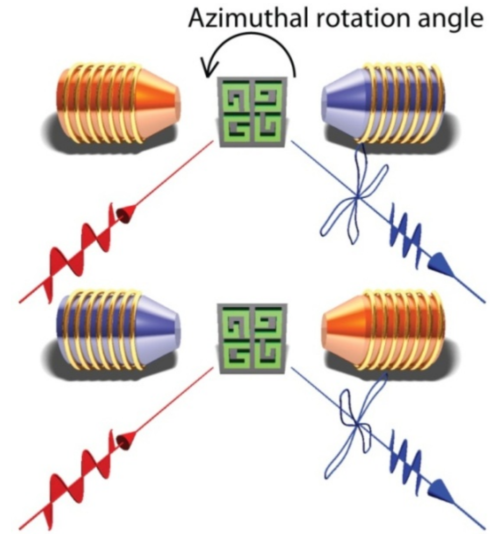


Upon azimuthal rotation of the sample, for linearly polarized light, the resulting SHG pattern exhibits a different sense of rotation and a different intensity depending on the direction of magnetization.

A large magneto-chiral effect?







The similarity between the SHG sensitivity to chirality in Au and to magnetism in Ni, suggests that **large magneto-chiral effects** could be observed in a these materials.

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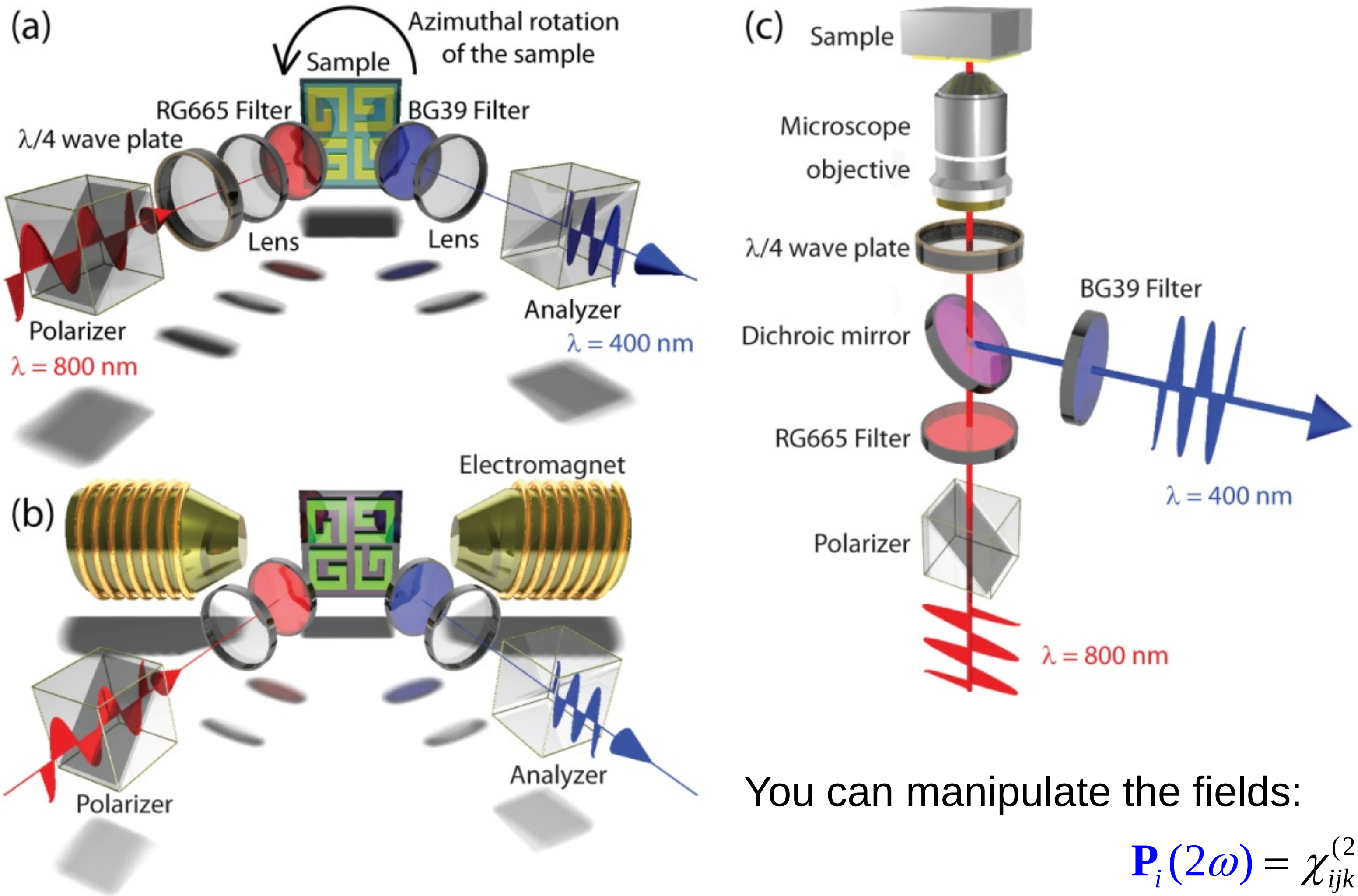
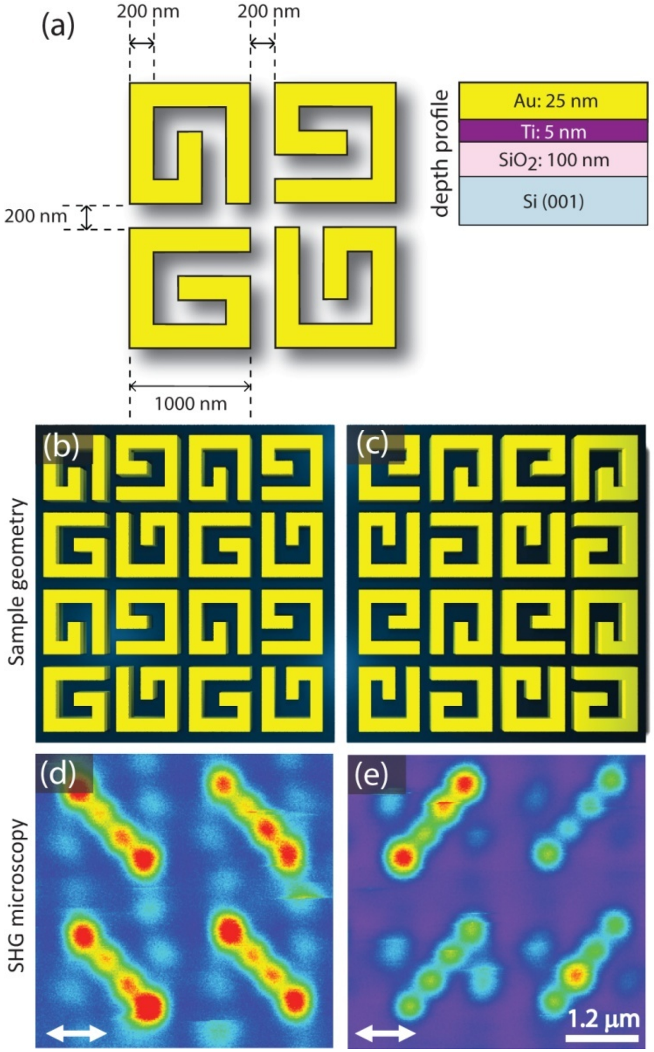
You can use symmetry to understand the SHG signal



You can manipulate the fields:

$$\mathbf{P}_i(2\omega) = \chi^{(2)}_{ijk} : \mathbf{E}_j(\omega)\mathbf{E}_k(\omega)$$

Near-field enhancements play an important role



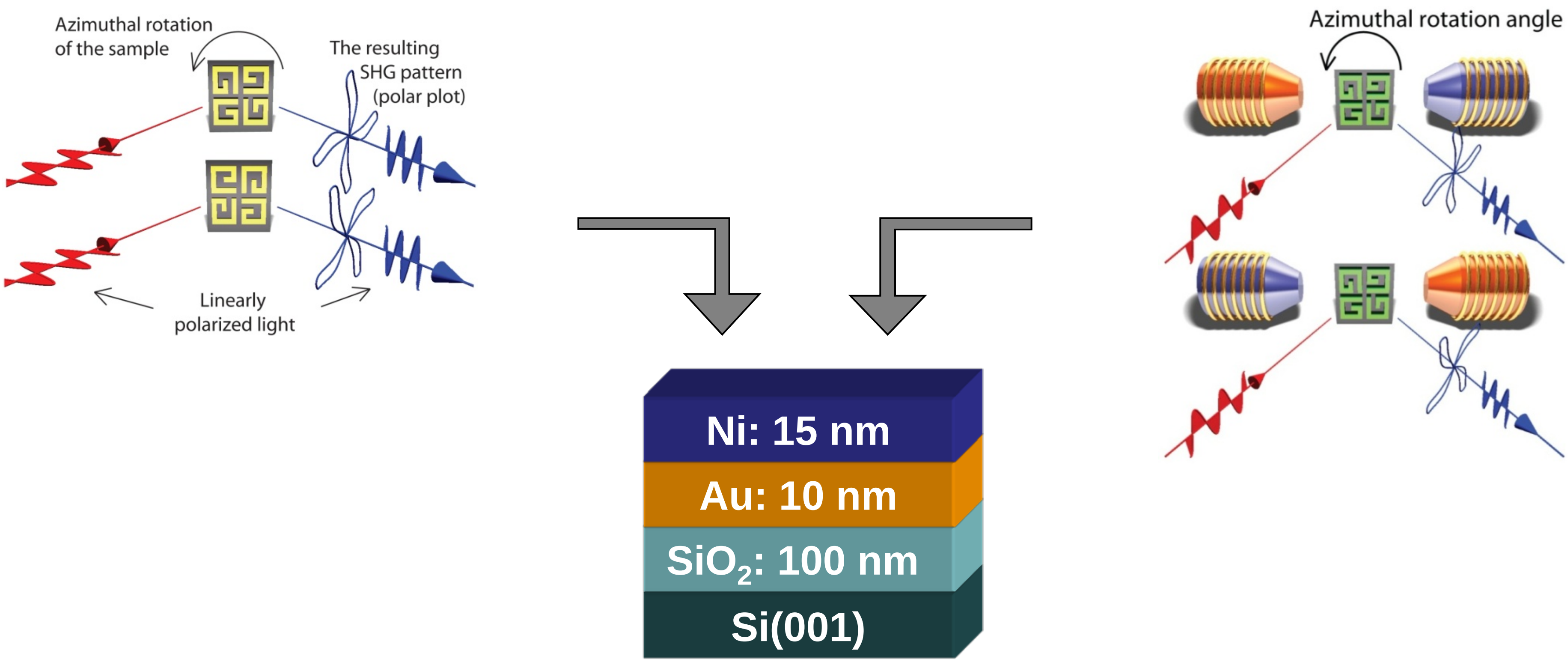
Rather than showing a G-shaped signal, the SHG microscopy reveals a pattern of clearly defined hotspots.

The white arrows indicate the direction of the linear polarization.

The color coded intensities increase from purple, through green, then yellow to red.

Ti was used as adhesion layer.

New properties lay on the road ahead



In every case, the interplay between symmetry and near-field enhancements will be the key to understanding them.

Thank you for your attention!

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URL: www.valev.org