2328-25

Preparatory School to the Winter College on Optics and the Winter College on Optics: Advances in Nano-Optics and Plasmonics

30 January - 17 February, 2012

Non linear optics of chiral materials

C. Sibilia

University Roma La Sapienza
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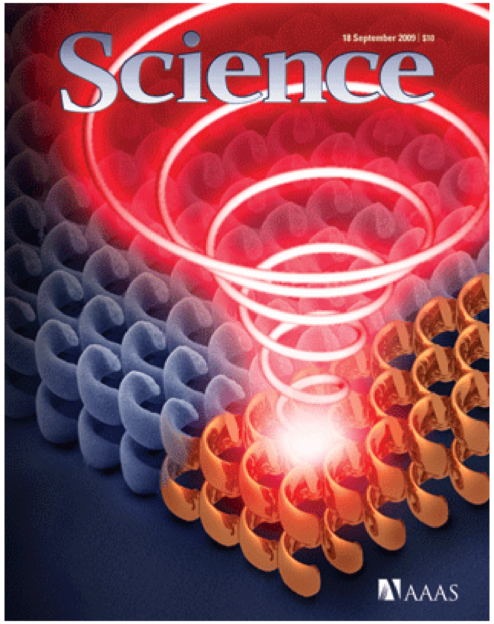
SAPIENZA
UNIVERSITÀ DI ROMA

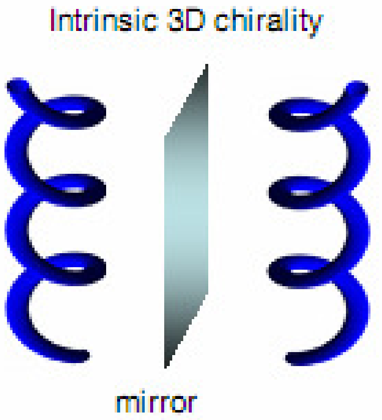
Nonlinear Optics of chiral materials

Concita Sibilia
Dipartimento SBAI-Universita’ di Roma La Sapienza

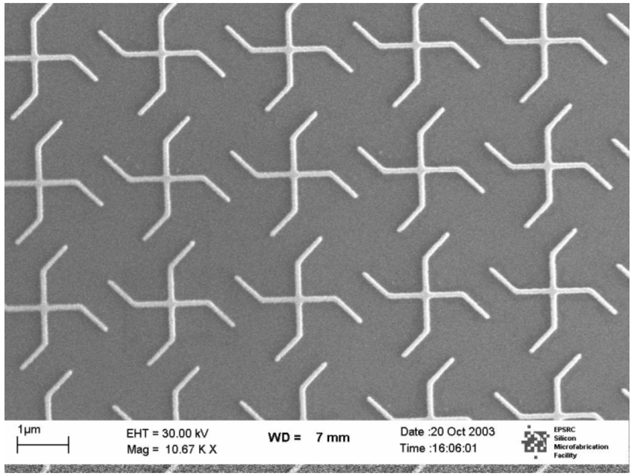
3D and 2D Chirality



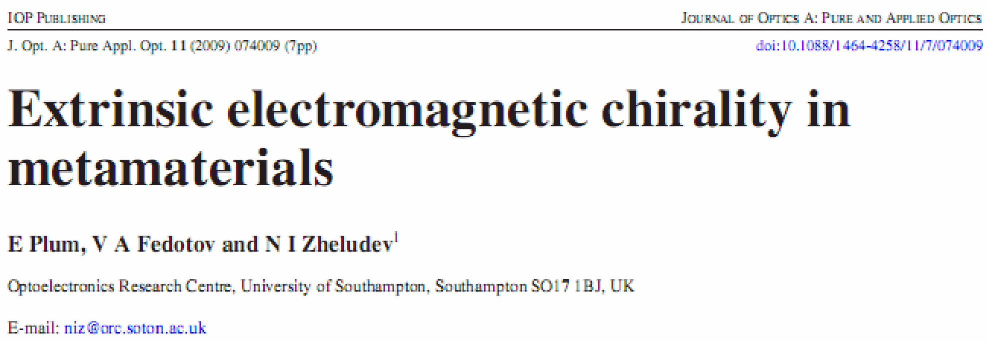
3D chiral metamaterial



Absence of mirror rotation axis



2D chiral metamaterial



IOP PUBLISHING JOURNAL OF OPTICS A: PURE AND APPLIED OPTICS

J. Opt. A: Pure Appl. Opt. 11 (2009) 074009 (7pp) doi:10.1088/1464-4258/11/7/074009

Extrinsic electromagnetic chirality in metamaterials

E Plum, V A Fedotov and N I Zheludev[1]

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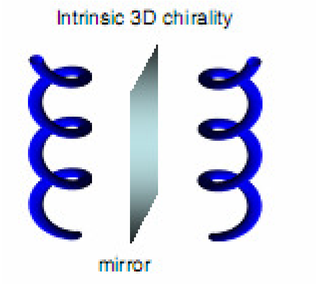
In the last years a lot of effort was devoted to the study on chiral metamaterials

Both 3D- and 2D-chiral metamaterials were studied

From N.Zheludev



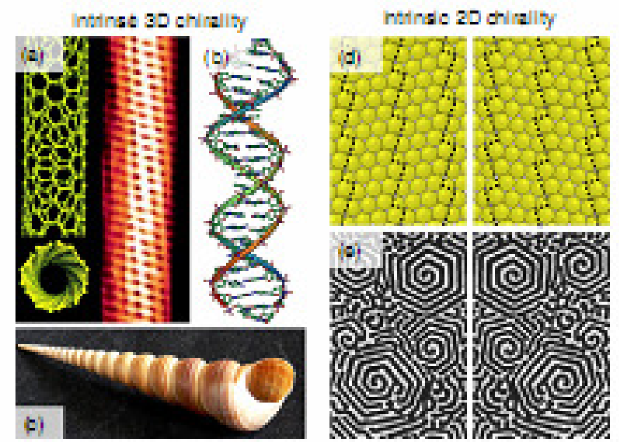
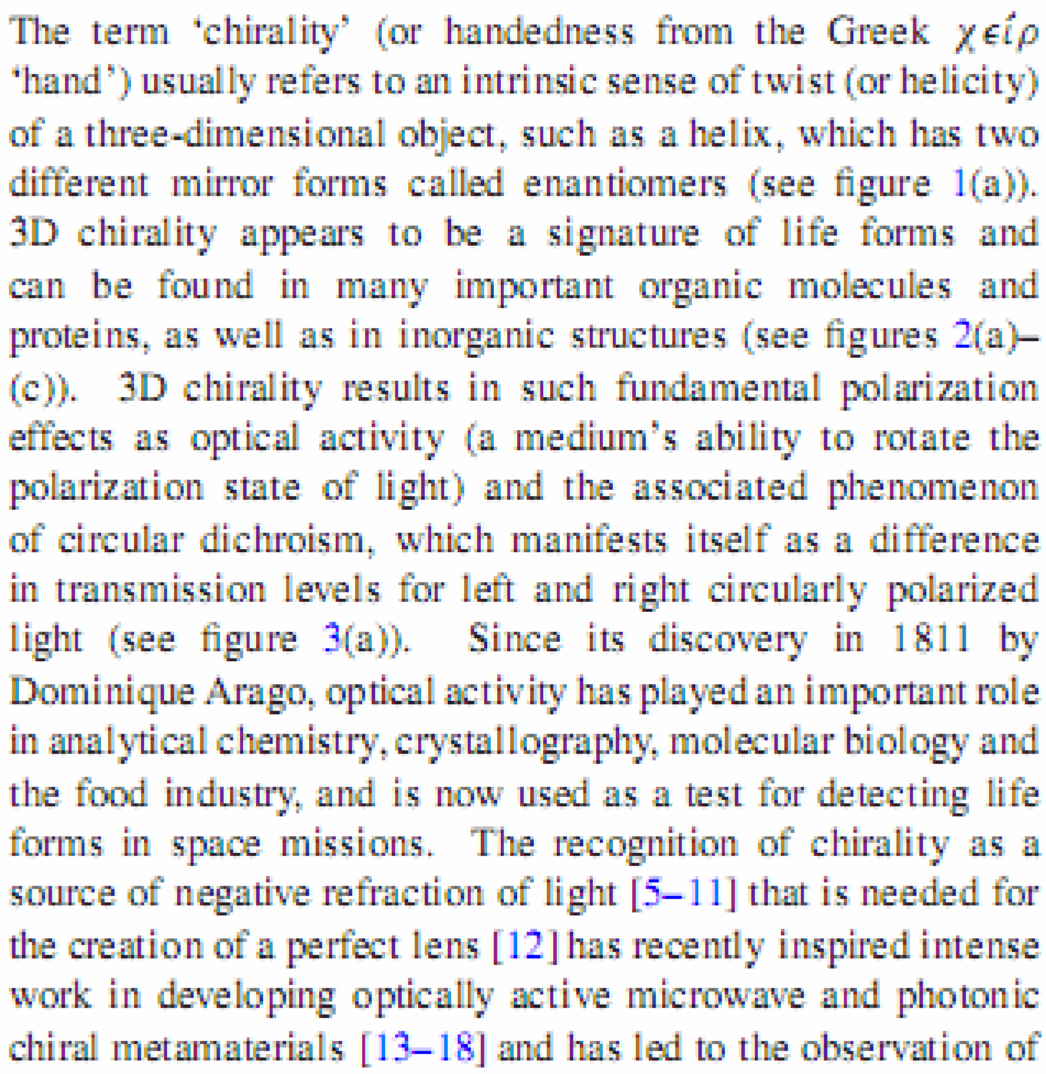


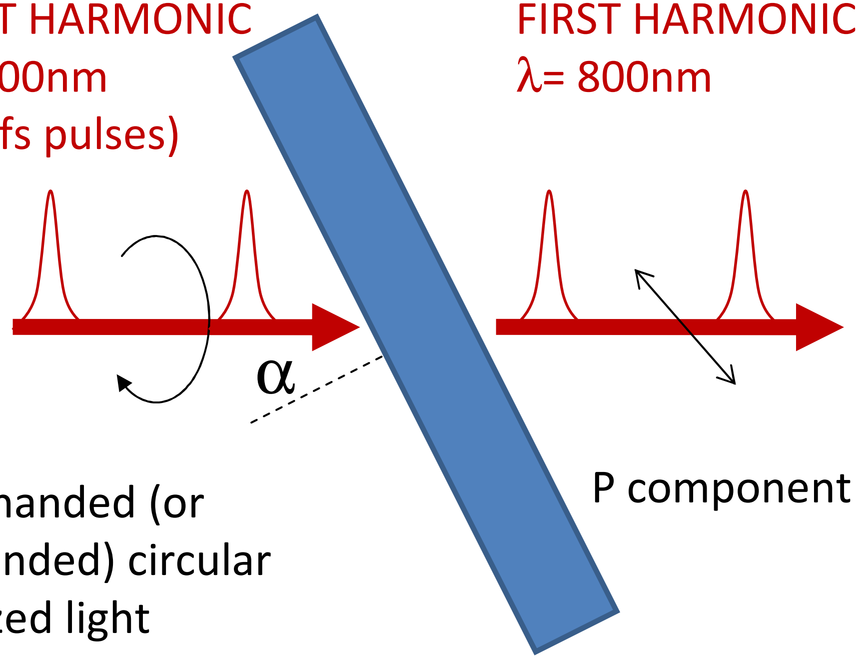
Figure 2. Examples of *intrinsically* chiral artificial and natural objects. 3D chirality: (a) single-wall carbon nanotube (structure and tunneling electron microscope image) [1], (b) DNA double helix [2] and (c) seashell from the Turritellidae family [3]. 2D chirality: (d) surface (643) of a gold monocrystal, (e) surface of a metal–metal eutectic [4].



The term ‘chirality’ (or handedness from the Greek $\chi\epsilon\acute{\iota}\rho$ ‘hand’) usually refers to an intrinsic sense of twist (or helicity) of a three-dimensional object, such as a helix, which has two different mirror forms called enantiomers (see figure 1(a)). 3D chirality appears to be a signature of life forms and can be found in many important organic molecules and proteins, as well as in inorganic structures (see figures 2(a)–(c)). 3D chirality results in such fundamental polarization effects as optical activity (a medium’s ability to rotate the polarization state of light) and the associated phenomenon of circular dichroism, which manifests itself as a difference in transmission levels for left and right circularly polarized light (see figure 3(a)). Since its discovery in 1811 by Dominique Arago, optical activity has played an important role in analytical chemistry, crystallography, molecular biology and the food industry, and is now used as a test for detecting life forms in space missions. The recognition of chirality as a source of negative refraction of light [5–11] that is needed for the creation of a perfect lens [12] has recently inspired intense work in developing optically active microwave and photonic chiral metamaterials [13–18] and has led to the observation of

Linear measurements

The measurements performed as a function of the incidence angle α



FIRST HARMONIC
λ= 800nm
(130fs pulses)

FIRST HARMONIC
λ= 800nm

Right-handed (or left-handed) circular polarized light

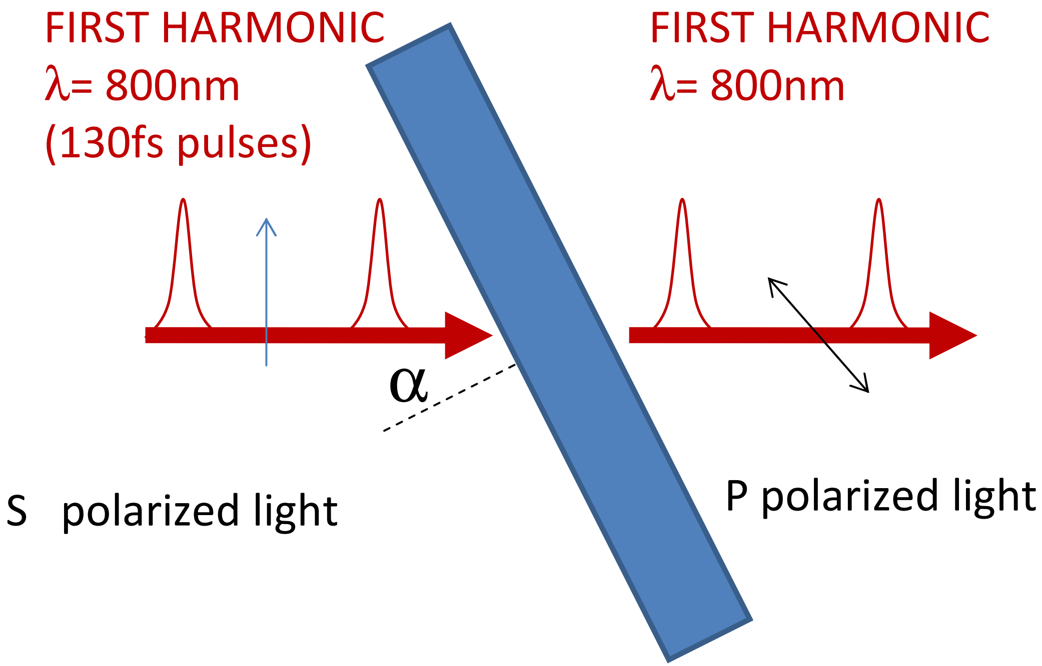
P component

circular dichroism (CD)

$$CD = \frac{I_L^\omega - I_R^\omega}{(I_L^\omega + I_R^\omega)/2}$$

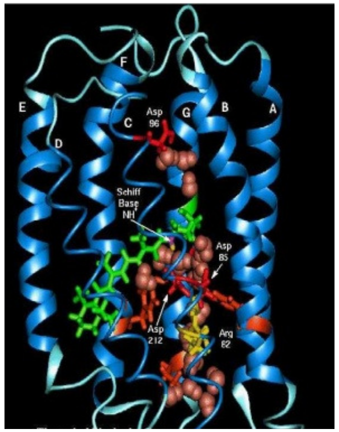
Linear measurements

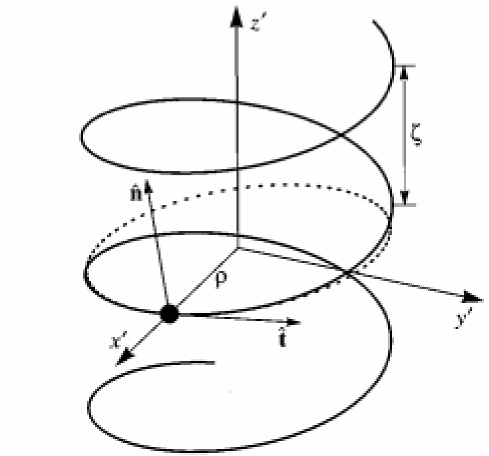
The measurements performed as a function of the incidence angle α



ORD - Rotation dispersion

As the electrons of chiral molecules are displaced from their equilibrium by the application of the electromagnetic field, they are forced
helical like paths





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

weak

Nonlinear optics, chirality, magneto-optics: a serendipitous road [Invited]

Andre Persoons[1,2,3,*]

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[2] College of Optical Sciences, University of Arizona, Tucson, Arizona 85721, USA
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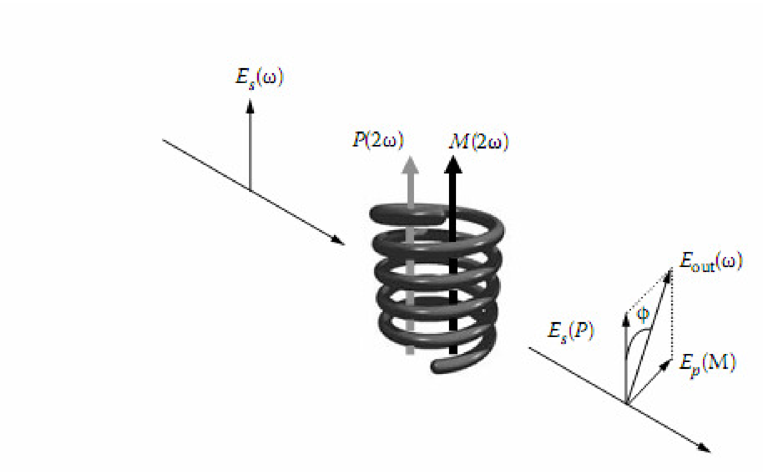
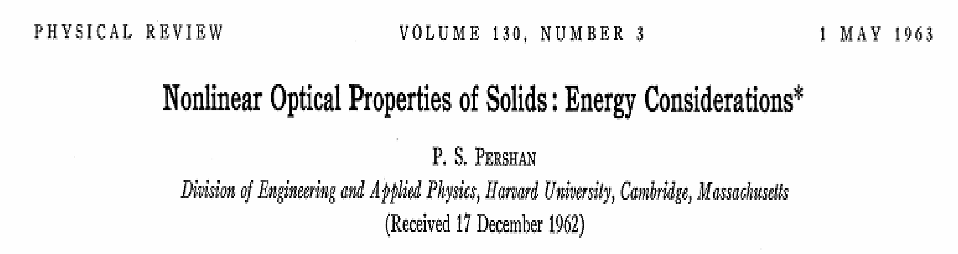
(C) 2011 OSA 1 May 2011 / Vol. 1, No. 1 / OPTICAL MATERIALS EXPRESS 5

Nonlinear Optical Activity



$$\chi^{(2)}_{IJK} = N \sum_{ijk} \langle (I \cdot i)(J \cdot j)(K \cdot k) \rangle \beta_{ijk}$$

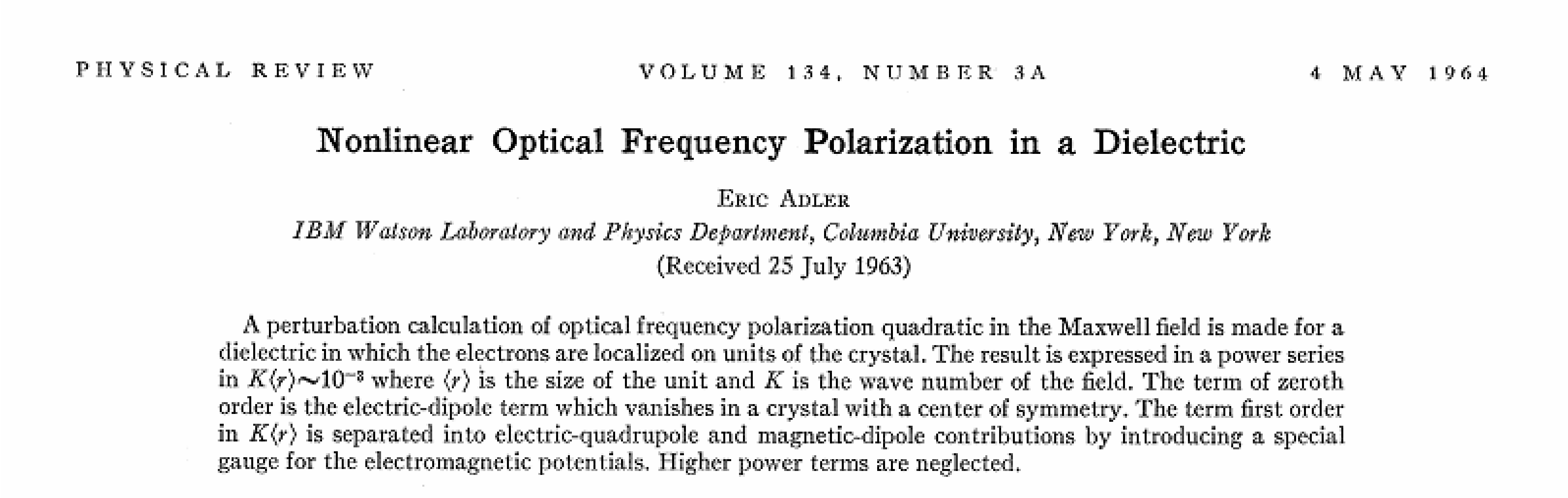


PHYSICAL REVIEW VOLUME 130, NUMBER 3 1 MAY 1963

Nonlinear Optical Properties of Solids: Energy Considerations*

P. S. PERSHAN
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

(Received 17 December 1962)



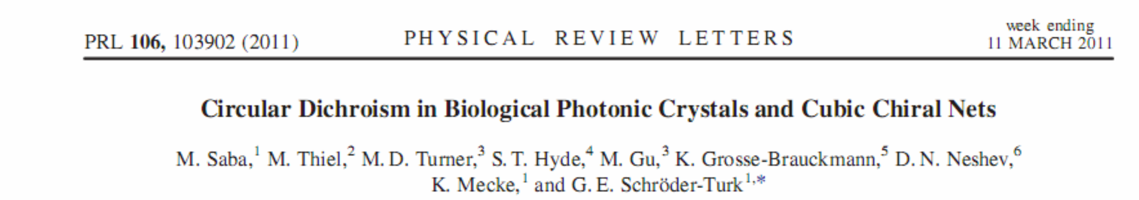
PHYSICAL REVIEW VOLUME 134, NUMBER 3A 4 MAY 1964

Nonlinear Optical Frequency Polarization in a Dielectric

ERIC ADLER
IBM Watson Laboratory and Physics Department, Columbia University, New York, New York

(Received 25 July 1963)

A perturbation calculation of optical frequency polarization quadratic in the Maxwell field is made for a dielectric in which the electrons are localized on units of the crystal. The result is expressed in a power series in $K\langle r\rangle\sim10^{-3}$ where $\langle r\rangle$ is the size of the unit and K is the wave number of the field. The term of zeroth order is the electric-dipole term which vanishes in a crystal with a center of symmetry. The term first order in $K\langle r\rangle$ is separated into electric-quadrupole and magnetic-dipole contributions by introducing a special gauge for the electromagnetic potentials. Higher power terms are neglected.



PRL **106,** 103902 (2011) PHYSICAL REVIEW LETTERS week ending 11 MARCH 2011

Circular Dichroism in Biological Photonic Crystals and Cubic Chiral Nets

M. Saba,[1] M. Thiel,[2] M. D. Turner,[3] S. T. Hyde,[4] M. Gu,[3] K. Grosse-Brauckmann,[5] D. N. Neshev,[6]
K. Mecke,[1] and G. E. Schröder-Turk[1,*]

Second-Order Nonlinear Optical Imaging of Chiral Crystals

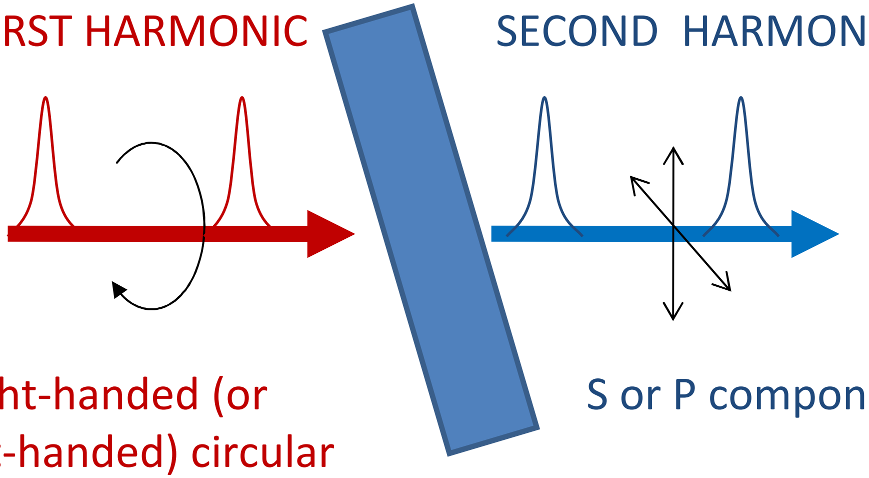
David J. Kissick, DebbieWanapun, and Garth J. Simpson

Department of Chemistry, Purdue University,West Lafayette, Indiana 47907;

Annu. Rev. Anal. Chem. 2011. 4:419–37

SHG as chirality detector

It is possible to investigate chirality via second harmonic generation experiments



FIRST HARMONIC

SECOND HARMONIC

Right-handed (or left-handed) circular polarized light

S or P component

One useful parameter is:
Second harmonic generation-circular dichroism (SHG-CD)

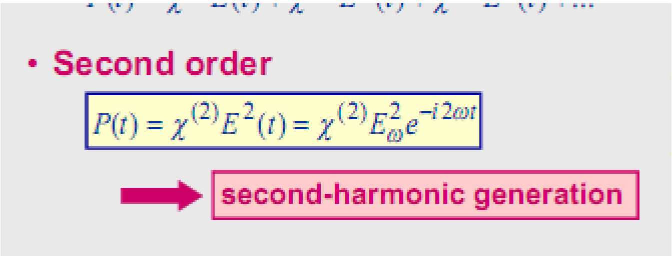
$$SHG-CD=\frac{I_L^{2\omega}-I_R^{2\omega}}{(I_L^{2\omega}+I_R^{2\omega})/2}$$

ORD

$$R(2\omega)=\frac{E_s(2\omega)}{E_p(2\omega)}=\frac{f_sE_p^2(\omega)+g_sE_s^2(\omega)+h_sE_p(\omega)E_s(\omega)}{f_pE_p^2(\omega)+g_pE_s^2(\omega)+h_pE_p(\omega)E_s(\omega)}$$

Verbiest, **Second-order Nonlinear Optical Characterization Techniques, Taylor & Francis (2009)**

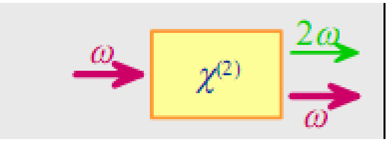
Intrinsic chirality



- **Second order**

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

$\Rightarrow$ second-harmonic generation



Multipolar Symmetries in SecondOrder Nonlinear Optics

– electric-dipole and higher-multipole nonlinearities –

-isotropic and centrosymmetric materials

Nonlinear susceptibility expansion

$$\chi(E) = \chi^{(1)} + \chi^{(2)} E + \chi^{(3)} EE + \dots$$

$$P(E) = \varepsilon_0 \left(\chi^{(1)} + \chi^{(2)} E + \chi^{(3)} E^2 + \dots\right) E$$

$$\vec{P}_{eff}(2\omega) = \vec{P}_D(2\omega) - \frac{1}{\omega} \vec{k}\, x \vec{M}(2\omega)$$

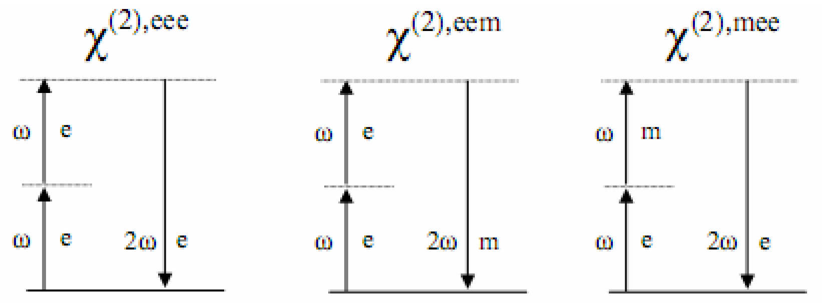
$$\vec{P}_D(2\omega) = \sum_{j,k} \chi_{ijk}^{(2)eee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{(2)eem} E_j(\omega) B_k(\omega)$$

Dipole dipole source

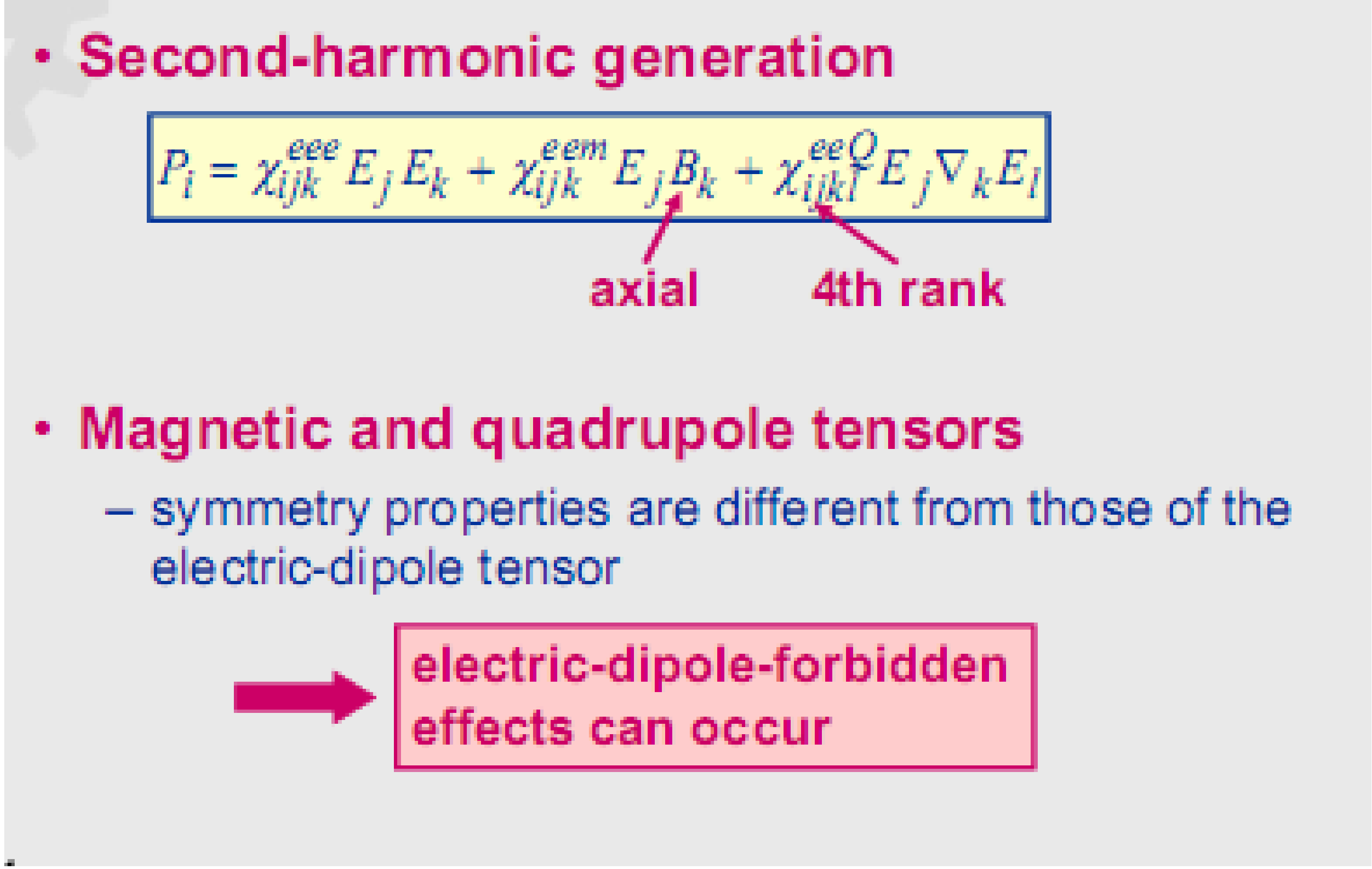
Magnetic dipole source

$$\vec{M}(2\omega) = \sum_{j,k} \chi_{ijk}^{(2)mee} E_j(\omega) E_k(\omega)$$

Nonlinear magnetization



Multipole symmetries



- **Second-harmonic generation**

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

axial **4th rank**

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

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

χ(2) Nonlinear Interaction

bulk

Phase matching ==

equal PHASE velocity

$$\eta = \frac{P^{(2\omega)}(L)}{P^{(\omega)}(0)} \propto \sin c^2\left(\frac{1}{2}\Delta kL\right) \Rightarrow \underline{\Delta k = 0} \Leftrightarrow n_o^{2\omega} \cancel{<} n_e^{\omega}$$

For nonhogenous media- Phc

P.M. (equal PHASE velocity),

For SH 2K_1 = K_2 ---- n(w) = n(2 w) ---if there is *geometrical dispersion*

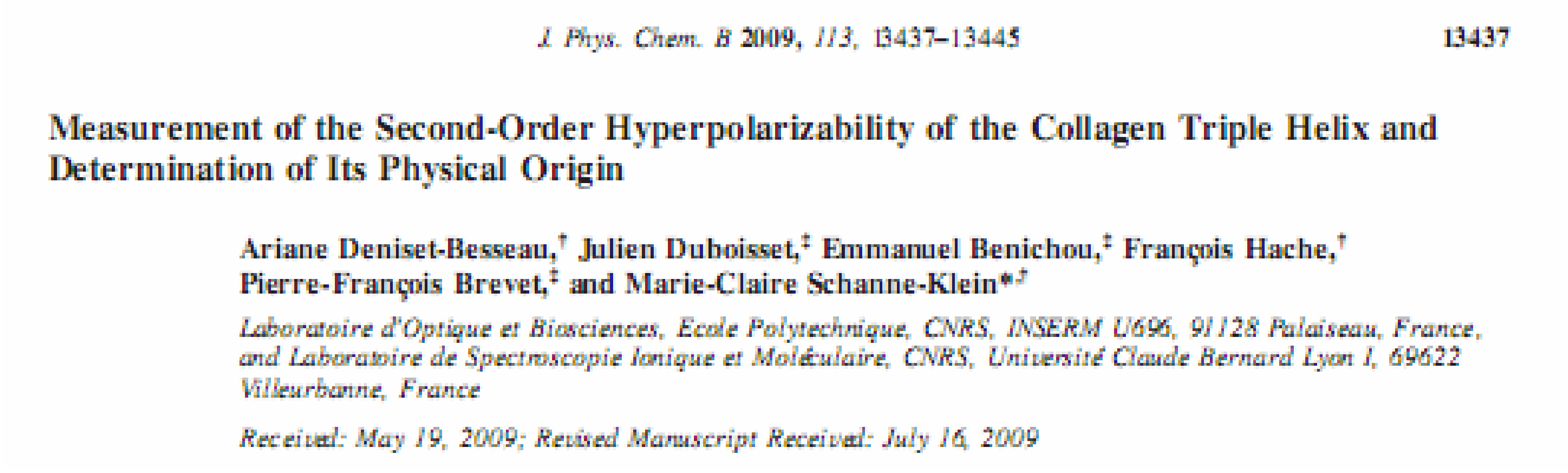
Thin films

No P.M. Interference between bound and free components (sourface and bulk)

At the nanoscale

No P.M. Field localization and overlap

materials



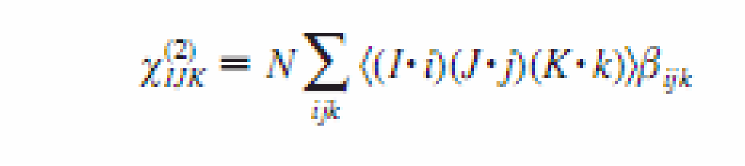
J. Phys. Chem. B 2009, 113, 13437–13445 13437

Measurement of the Second-Order Hyperpolarizability of the Collagen Triple Helix and Determination of Its Physical Origin

Ariane Deniset-Besseau,[†] Julien Duboisset,[‡] Emmanuel Benichou,[‡] François Hache,[†] Pierre-François Brevet,[‡] and Marie-Claire Schanne-Klein*[,†]

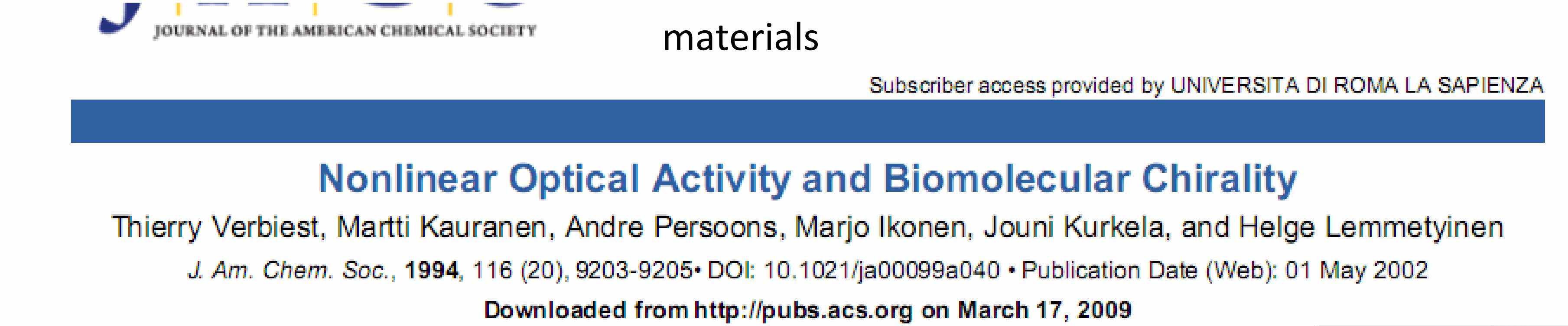
Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, INSERM U696, 91128 Palaiseau, France, and Laboratoire de Spectroscopie Ionique et Moléculaire, CNRS, Université Claude Bernard Lyon 1, 69622 Villeurbanne, France

Received: May 19, 2009; Revised Manuscript Received: July 16, 2009



$$\chi^{(2)}_{IJK} = N \sum_{ijk} \langle (I \cdot i)(J \cdot j)(K \cdot k) \rangle \beta_{ijk}$$

materials



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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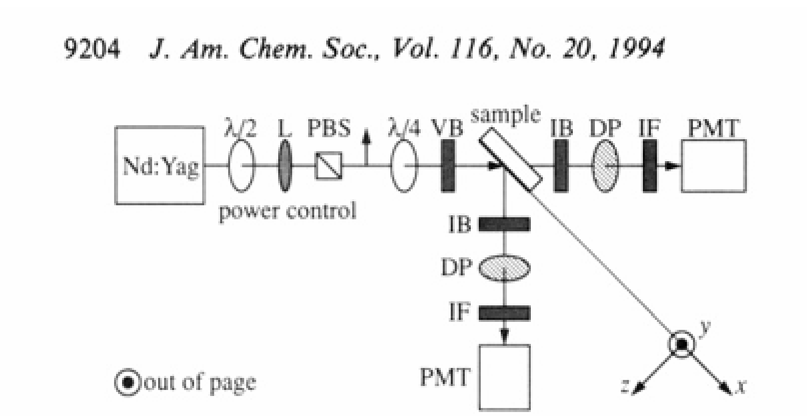
Nonlinear Optical Activity and Biomolecular Chirality

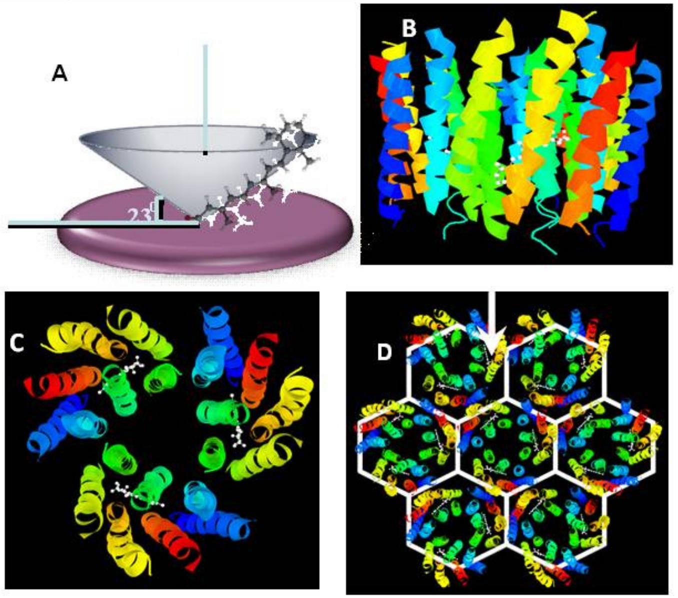
Thierry Verbiest, Martti Kauranen, Andre Persoons, Marjo Ikonen, Jouni Kurkela, and Helge Lemmetyinen

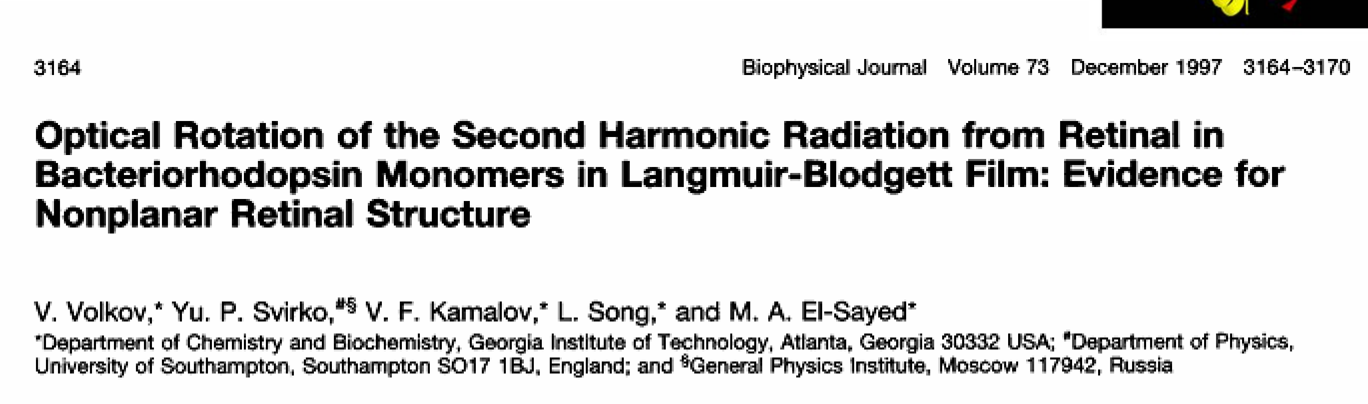
J. Am. Chem. Soc., **1994**, 116 (20), 9203-9205• DOI: 10.1021/ja00099a040 • Publication Date (Web): 01 May 2002

Downloaded from http://pubs.acs.org on March 17, 2009



9204 *J. Am. Chem. Soc., Vol. 116, No. 20, 1994*





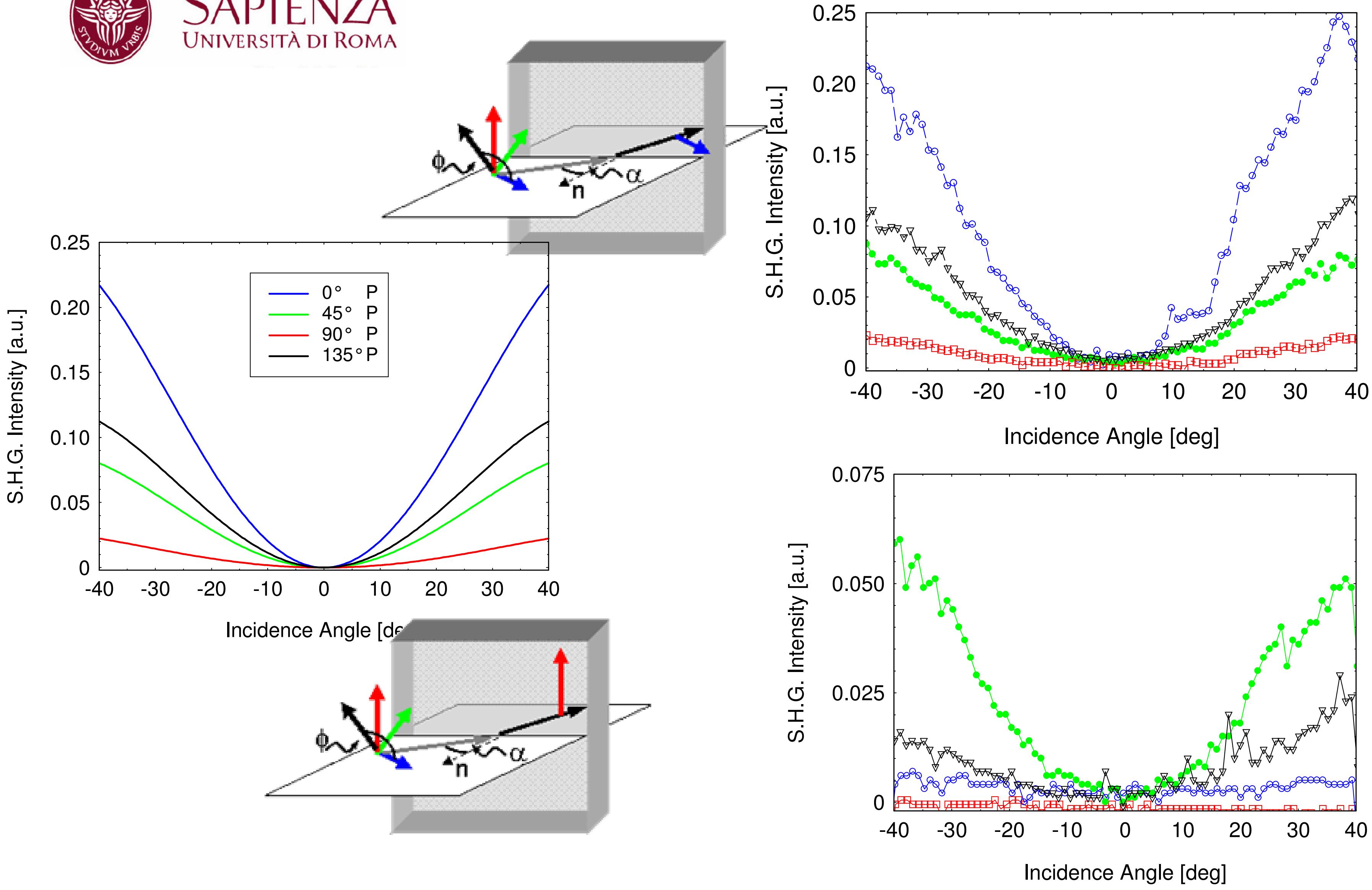
3164 Biophysical Journal Volume 73 December 1997 3164–3170

Optical Rotation of the Second Harmonic Radiation from Retinal in Bacteriorhodopsin Monomers in Langmuir-Blodgett Film: Evidence for Nonplanar Retinal Structure

V. Volkov,* Yu. P. Svirko,#§ V. F. Kamalov,* L. Song,* and M. A. El-Sayed*

*Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 USA; #Department of Physics, University of Southampton, Southampton SO17 1BJ, England; and §General Physics Institute, Moscow 117942, Russia

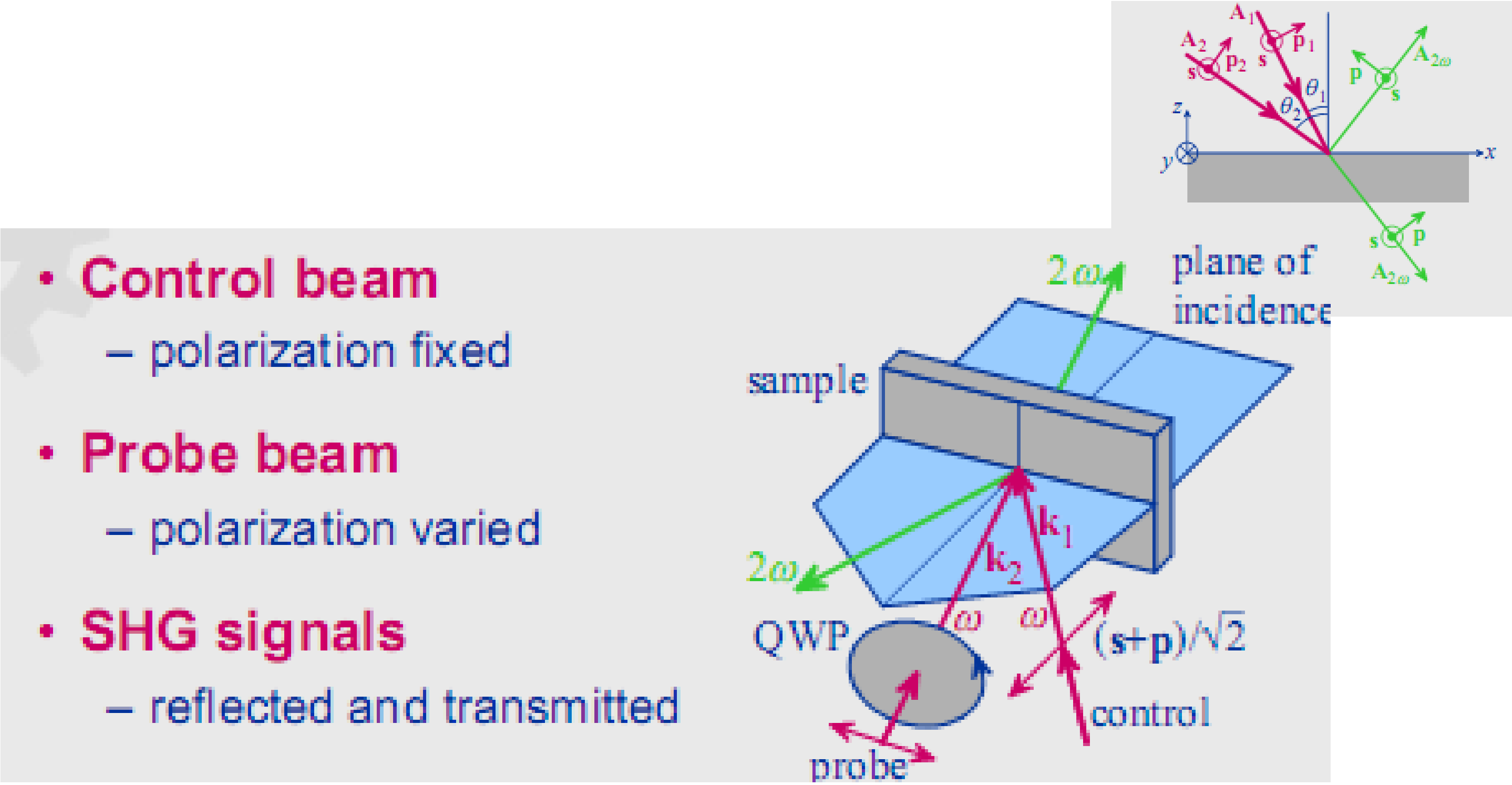
Maker Fringes on BR



$d_{15}= d_{24}=$ 2.02 pm/V , $d_{31}= d_{32}=$ 2.44 pm/V , $d_{33}=$ 4.70 pm/V, as well as the chiral coefficients $d_{25}= - d_{14}=$ 0.34 pm/V.

M.Larciprete et al. APL 2009

Two beams



- **Control beam**
  - polarization fixed
- **Probe beam**
  - polarization varied
- **SHG signals**
  - reflected and transmitted

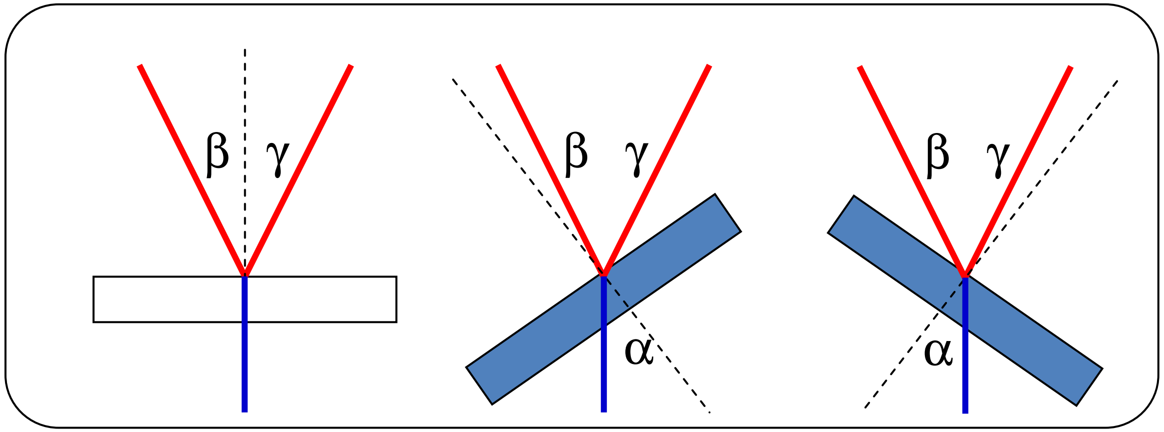
M.Kauranen et al
Progress in Optics

Second Harmonic Generation – Noncollinear case

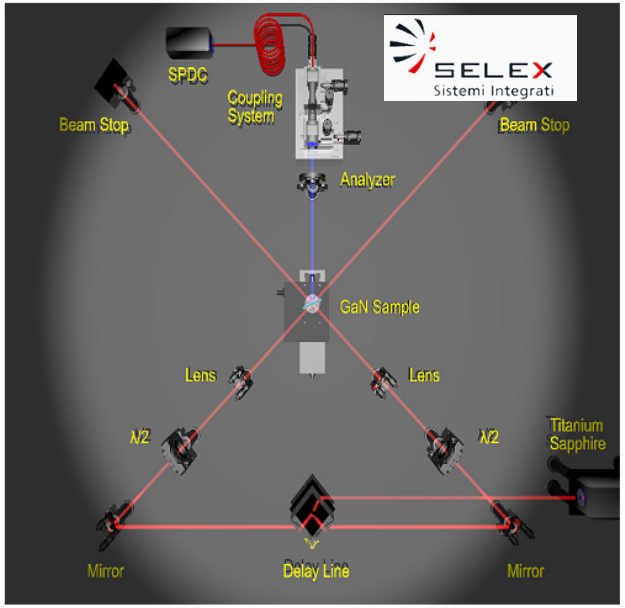
$$W_{\omega1+\omega2}(\alpha)=\left(\frac{512\pi^3}{A}\right)\overbrace{(t_{\omega1})^2\cdot(t_{\omega2})^2}^{\text{Transmission Coefficient at }\omega\text{ for pump 1 \& 2}}\cdot\underset{\substack{\uparrow\\ \text{Transmittance at }2\omega}}{T_{\omega1+\omega2}}\cdot\overbrace{W_{\omega1}\cdot W_{\omega2}}^{\text{Power of the field at }\omega\text{ for pump 1 \& 2}}\frac{\sin^2(\Psi_{SHG}(\alpha))}{\left[n_{\omega1}\cdot n_{\omega2}-n^2_{\omega1+\omega2}\right]^2}\left(d_{eff}(\alpha)\right)^2$$

$$\Psi_{SHG}=\left(\frac{\pi L}{2}\right)\left(\frac{2}{\lambda}\right)\left[n_{\omega1}\cdot cos(\alpha'_{\omega1})+n_{\omega2}\cdot cos(\alpha'_{\omega2})-2n_{\omega1+\omega2}\cdot cos(\alpha'_{\omega1+\omega2})\right]$$

✓ The difference between the two incidence angles is set to a fixed value (18°)



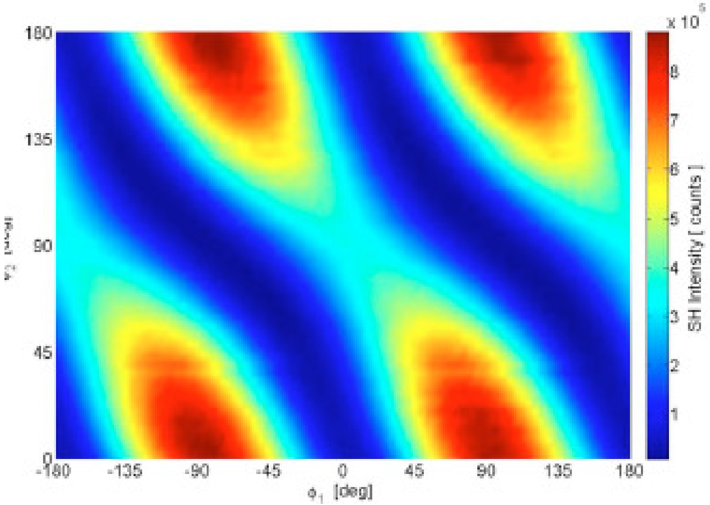
Polarization chart



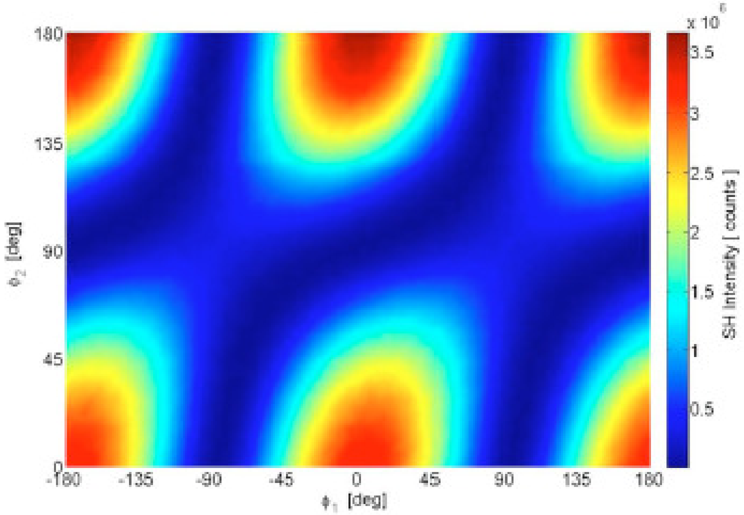
- At a fixed incidence angle, the generated signal is investigated by varying the polarization state of both fundamental beams.

- Example: GaN slab, ~300nm thick

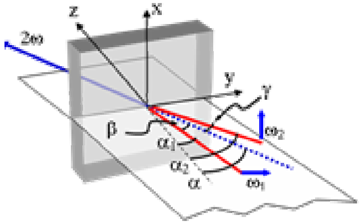
S-polarized SH signal



P-polarized SH signal

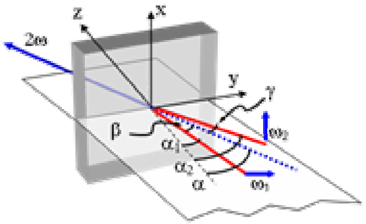


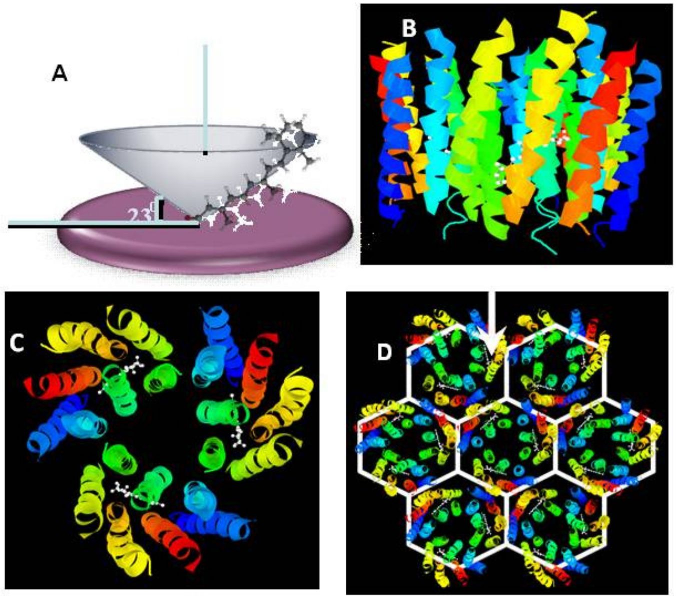
F.A.Bovino
Selex-SI-
Genova

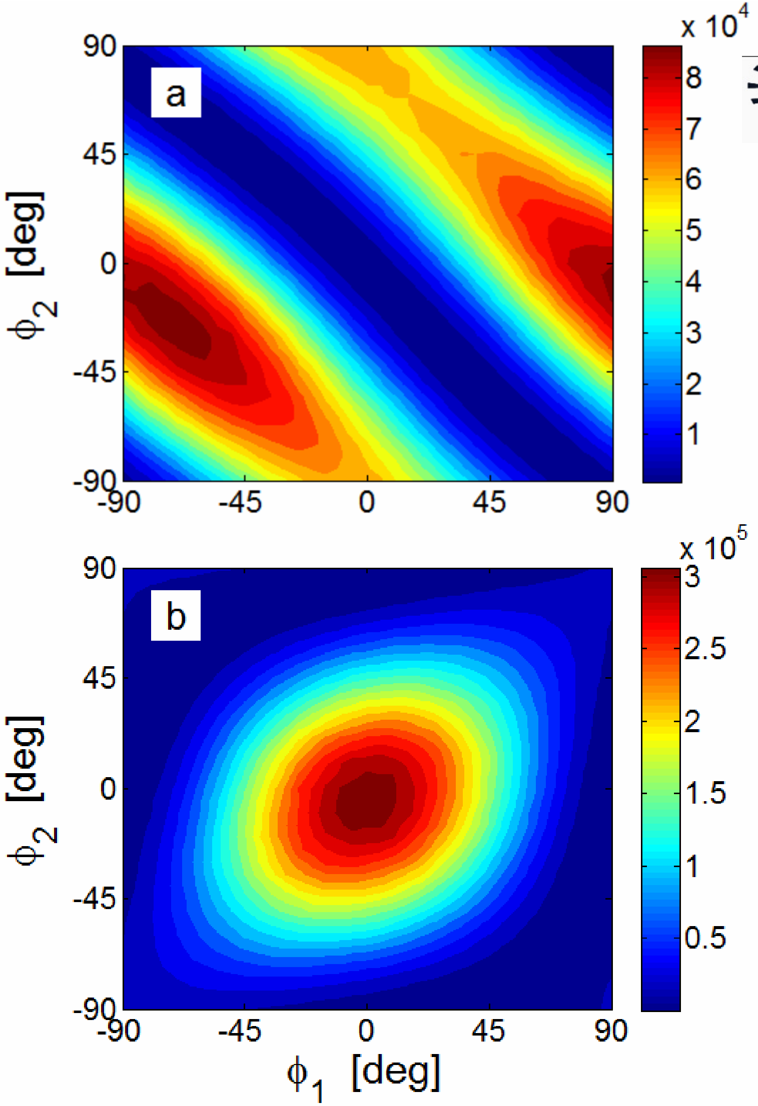


M.C.Larciprete,F.A.Bovino, M.Giardina, A.Belardini, M.Centini, C.Sibilia, M.Bertolotti, A. Passaseo and V.Tasco, "Mapping the nonlinear optical susceptibility by noncollinear second-harmonic generation", Optics Letters, Vol. 34, pp.2189-2191 (2009)

Polarization Chart in noncollinear SHG-BR







F.A Bovino et al- Selex-SI-Italy

Power of SH Signal

$$W_{\omega1+\omega2}(\alpha)=\left(\frac{512\pi^3}{A}\right)(t_{\omega1})^2\cdot(t_{\omega2})^2\cdot T_{\omega1+\omega2}\cdot W_{\omega1}\cdot W_{\omega2}\frac{\sin^2(\Psi_{SHG}(\alpha))}{\left[n_{\omega1}\cdot n_{\omega2}-n^2_{\omega1+\omega2}\right]^2}\left(|d^{(2)}_{eff}(\alpha)|\right)^2$$

$$d^{(2)}_{eff}=\left(\hat{p}_{out}\right)\left(d_{il}{}^{(eee)}\right)(\hat{p}^{1\,e}_{in})(\hat{p}^{2\,e}_{in})+$$
$$\left(\hat{p}_{out}\right)\left(d_{il}{}^{(eem1)}\right)(\hat{p}^{1\,e}_{in})(\hat{p}^{2\,m}_{in})+\left(\hat{p}^{e}_{out}\right)\left(d_{il}{}^{(eem2)}\right)(\hat{p}^{1\,m}_{in})(\hat{p}^{2\,e}_{in})+$$
$$\left(\hat{p}_{out}\right)xK\left(d_{il}{}^{(mee)}\right)(\hat{p}^{1\,e}_{in})(\hat{p}^{2\,e}_{in})$$

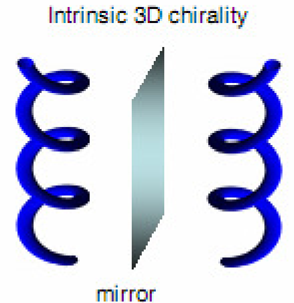
$$d_{il}=\frac{\hat{\chi}^{(2)}_{ijk}}{2}$$

$\hat{p}_{out}$: *polarization versor of output sh signal*

$\hat{p}^{1}_{in}$: *polarization versor of input pump 1 signal*

$\hat{p}^{2}_{in}$: *polarization versor of input pump 2 signal*

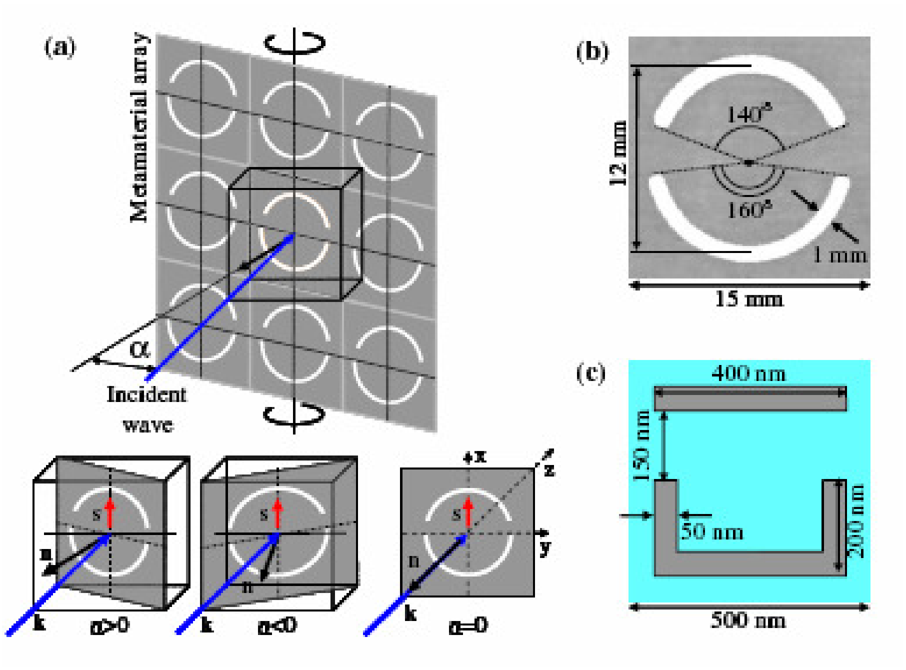
3p



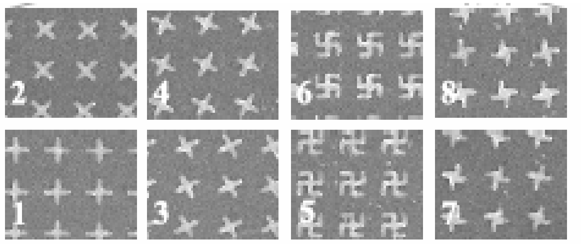
$$\begin{pmatrix} 0 & 0 & 0 & d^{eee}_{14} & d^{eee}_{15} & 0 \\ 0 & 0 & 0 & d^{eee}_{24} & d^{eee}_{25} & 0 \\ d^{eee}_{31} & d^{eee}_{32} & d^{eee}_{33} & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 & d^{eem}_{14} & d^{eem}_{15} & 0 \\ 0 & 0 & 0 & d^{eem}_{24} & d^{eem}_{25} & 0 \\ d^{eem}_{31} & d^{eem}_{32} & d^{eem}_{33} & 0 & 0 & d^{eem}_{36} \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 & d^{mee}_{14} & d^{mee}_{15} & 0 \\ 0 & 0 & 0 & d^{mee}_{24} & d^{mee}_{25} & 0 \\ d^{mee}_{31} & d^{mee}_{32} & d^{mee}_{33} & 0 & 0 & \end{pmatrix}$$

Extrinsic Chirality

E. Plum, PRL 102,113902 (2009)

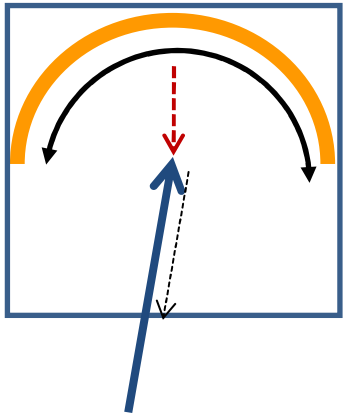


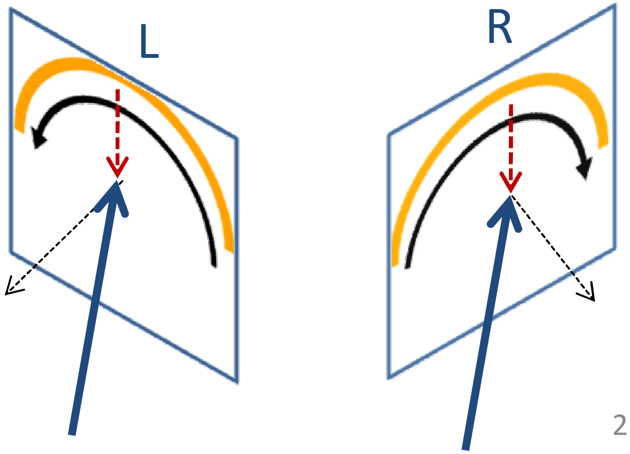
S.N. Volkov, PRA 79, 043819 (2009)



Extrinsic chirality: A non-chiral element breaks the symmetry when is tilted with respect the incidence light. The element thus assumes a chiral behavior

no-chirality

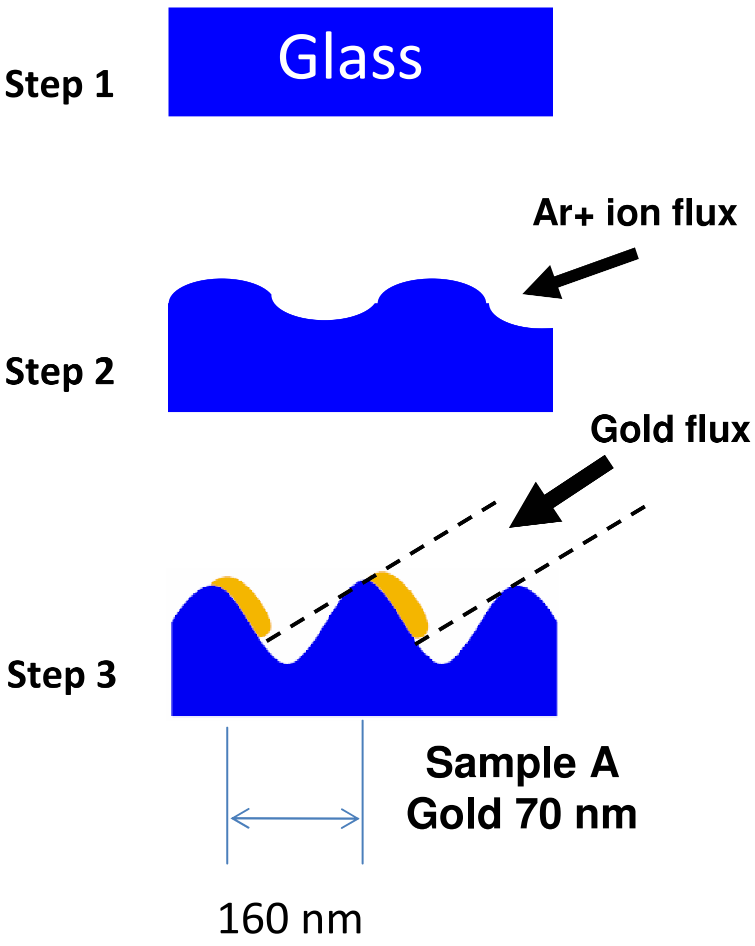




Extrinsic Chirality

Test sample fabrication – Sample A

Low cost self assembling procedure



Step 1

Glass

Step 2

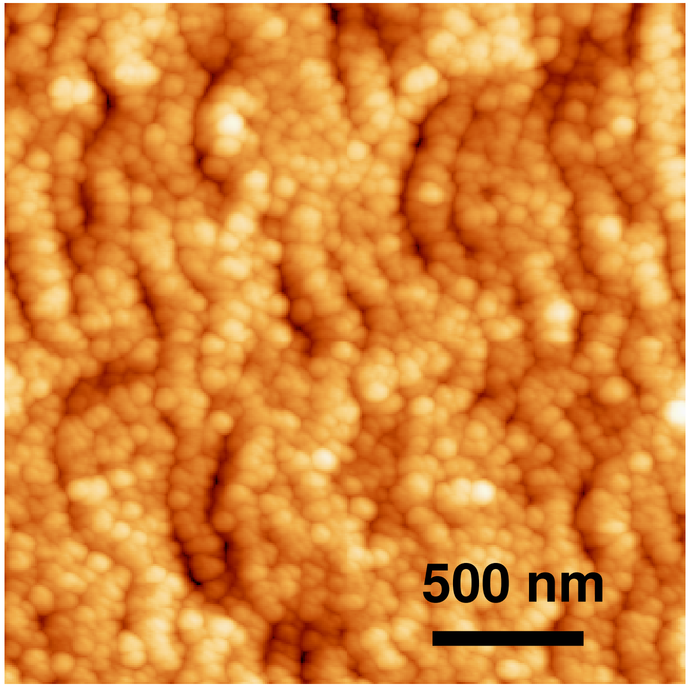
Ar+ ion flux

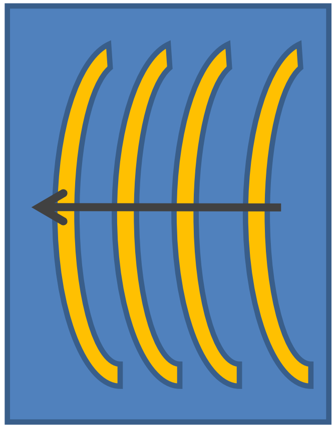
Gold flux

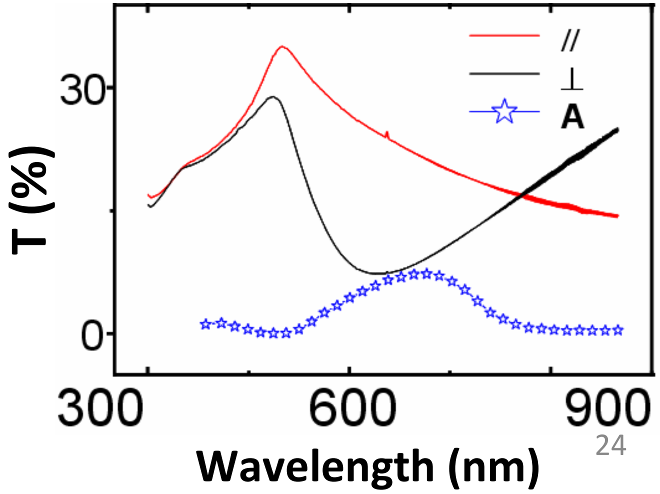
Step 3

Sample A
Gold 70 nm

160 nm

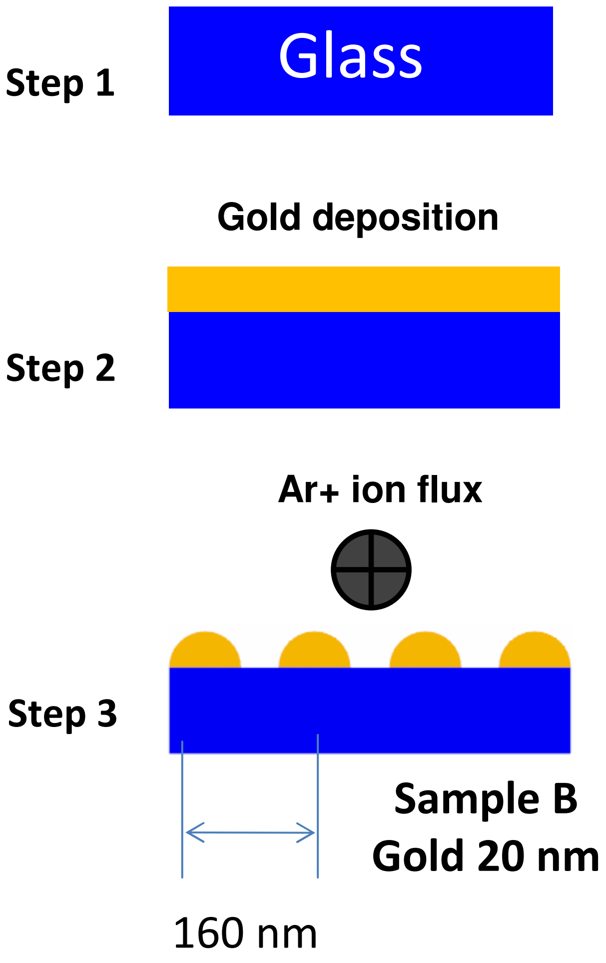






Reference sample fabrication – Sample B

Low cost self assembling procedure



Step 1

Glass

Gold deposition

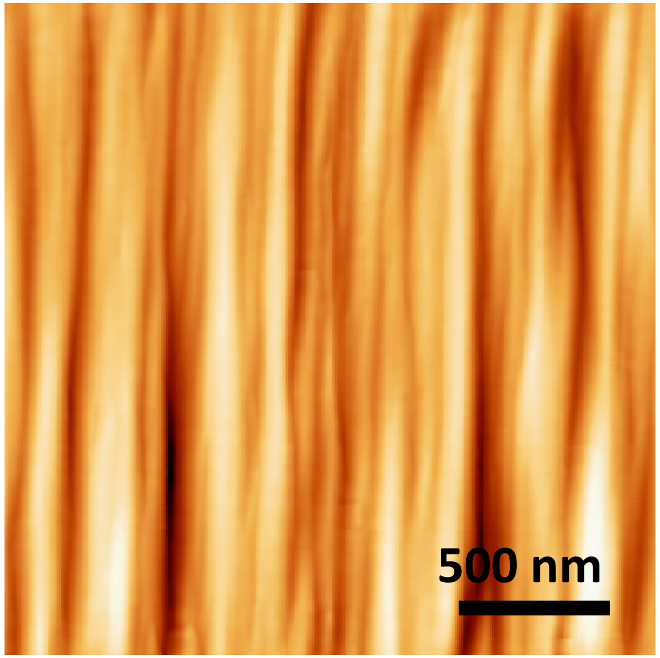
Step 2

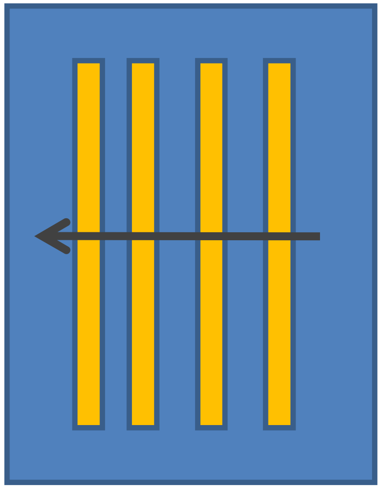
Ar+ ion flux

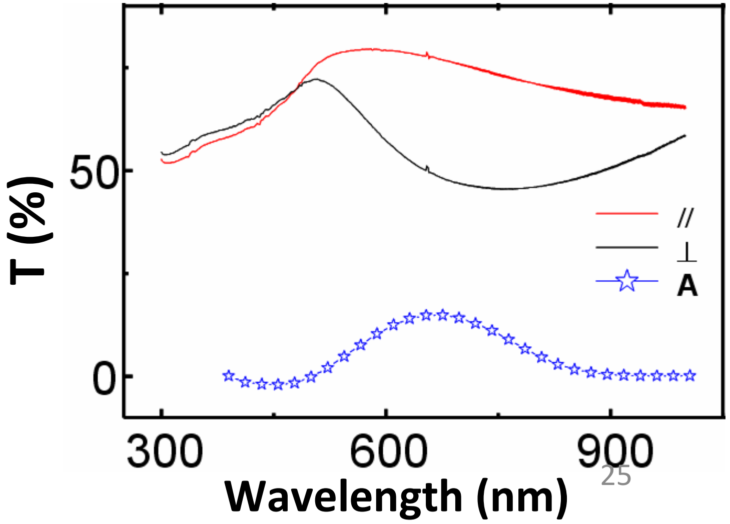
Step 3

Sample B
Gold 20 nm

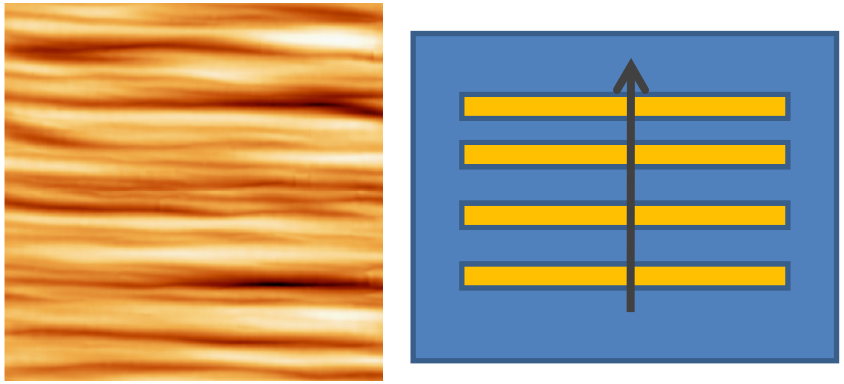
160 nm

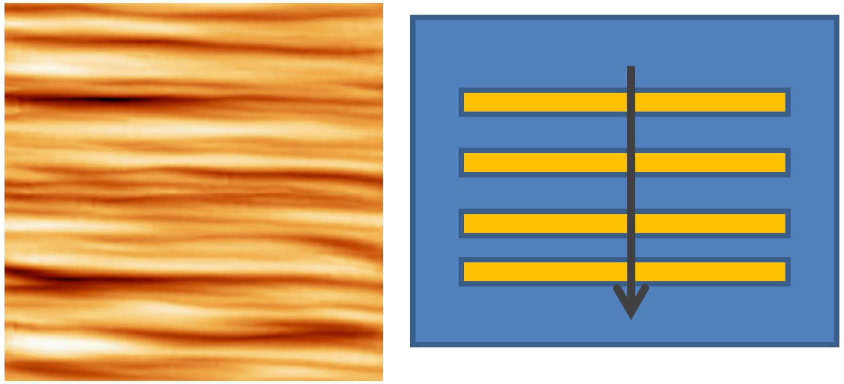


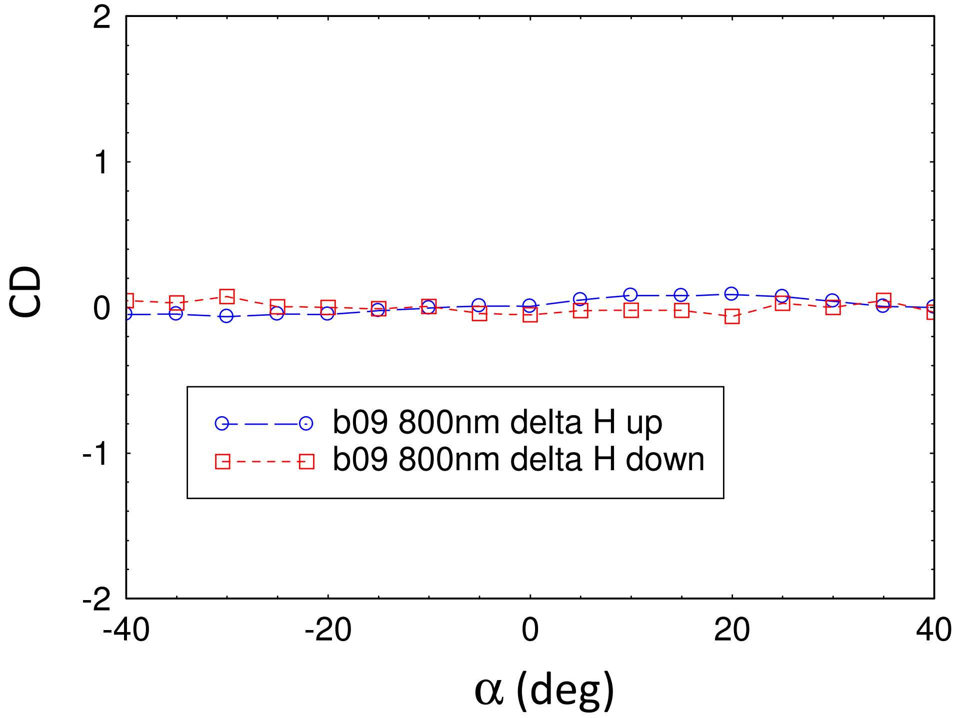




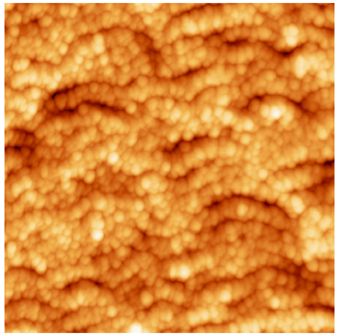
Linear measurements on sample B - P pol

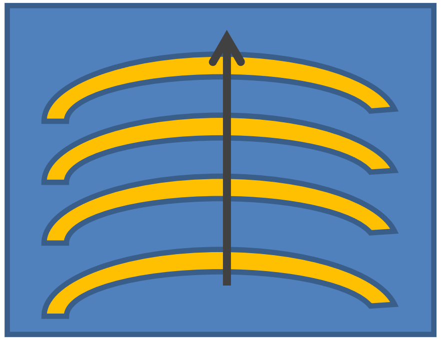


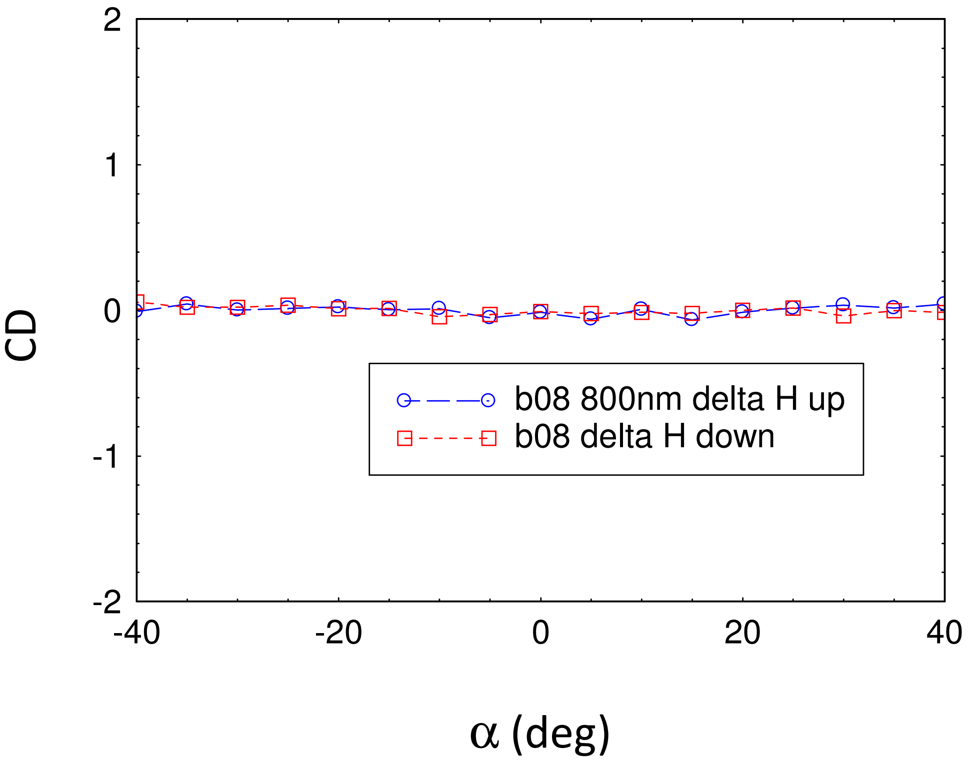


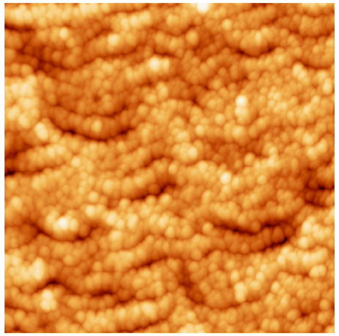


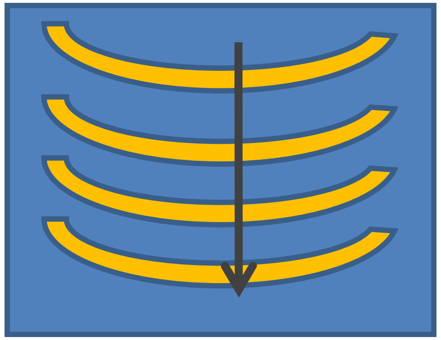
Linear measurements on sample A - P pol





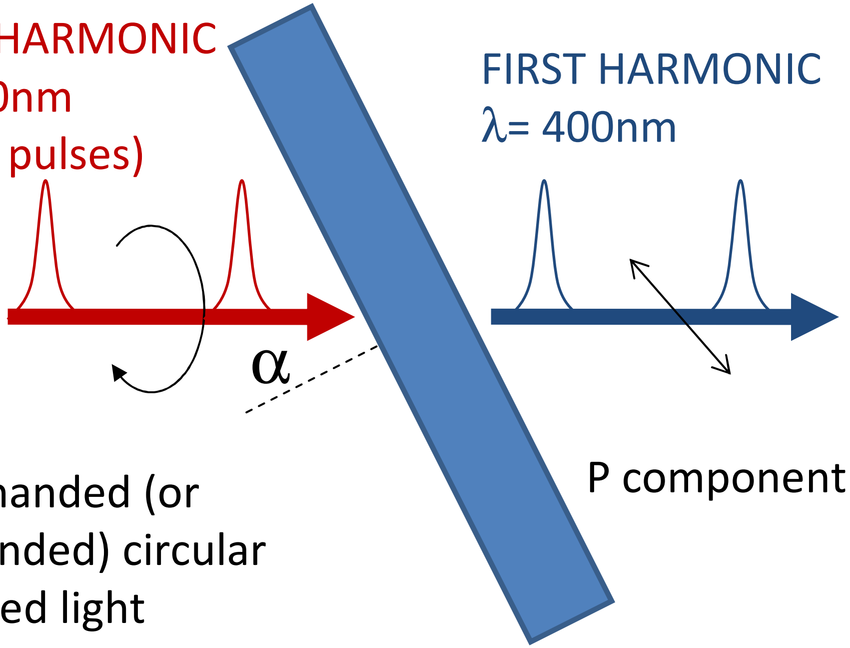






SHG measurements – P pol

The measurements were performed as a function of the incidence angle α



FIRST HARMONIC
λ= 800nm
(130fs pulses)

FIRST HARMONIC
λ= 400nm

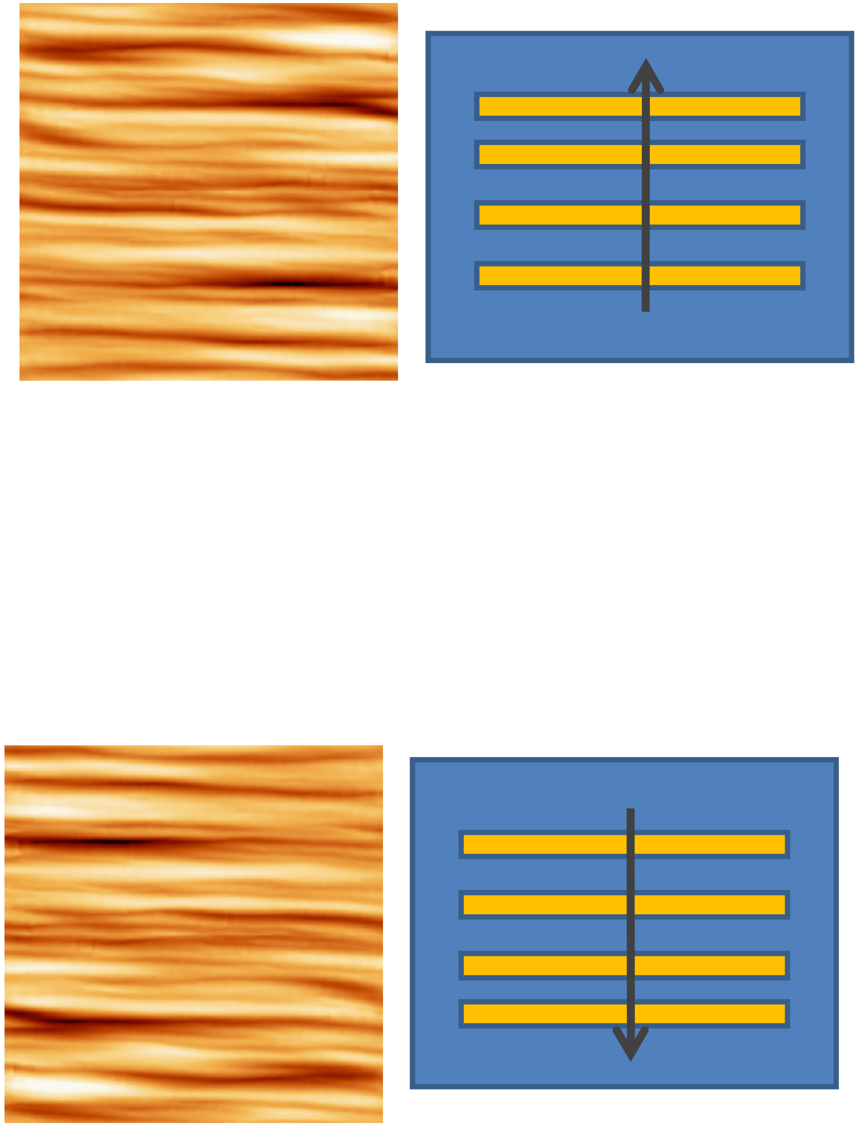
Right-handed (or
left-handed) circular
polarized light

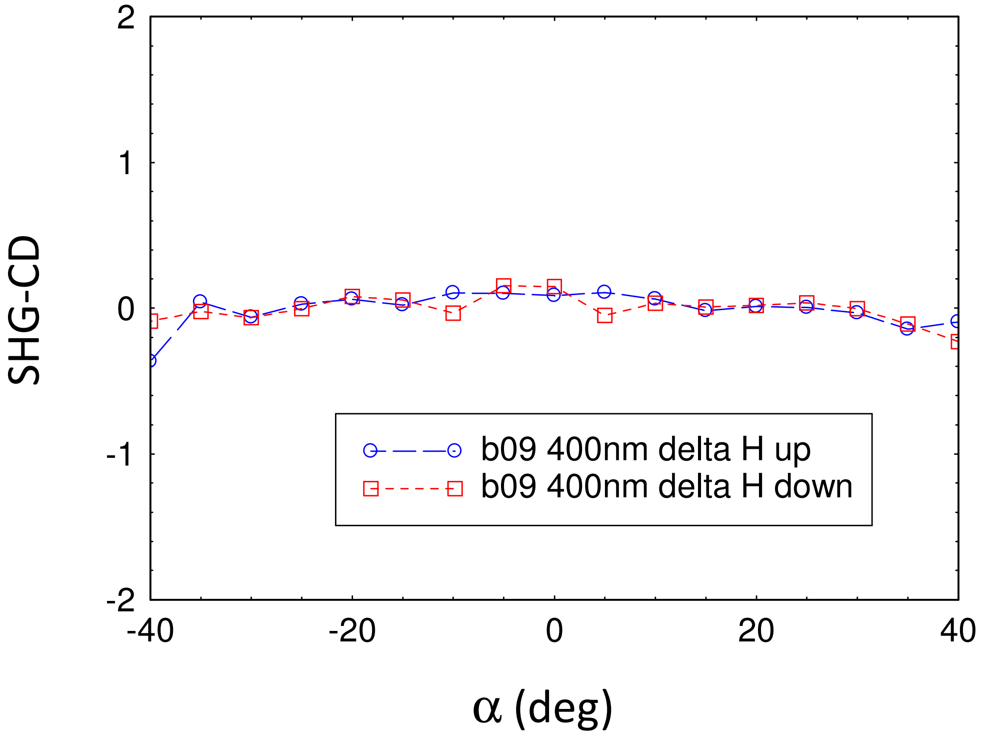
P component

Second harmonic
generation - circular
dichroism (SHG-CD)

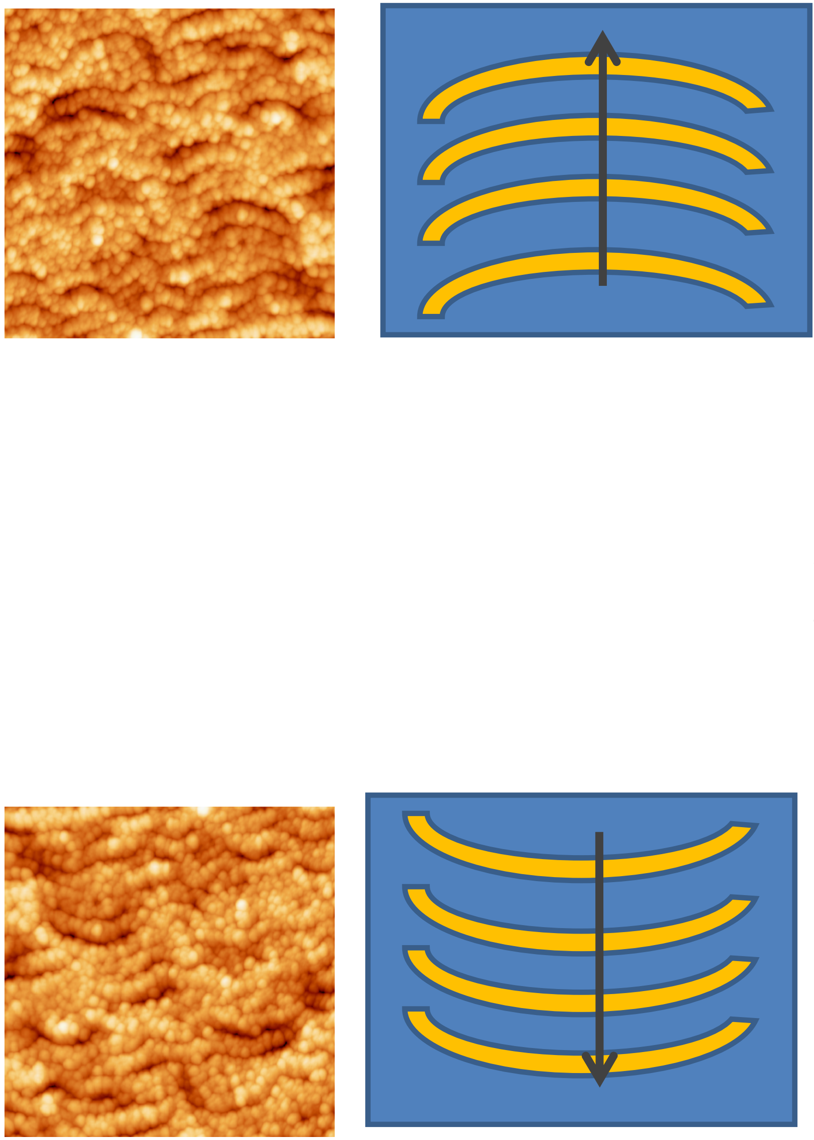
$$SHG-CD=\frac{I_L^{2\omega}-I_R^{2\omega}}{(I_L^{2\omega}+I_R^{2\omega})/2}$$

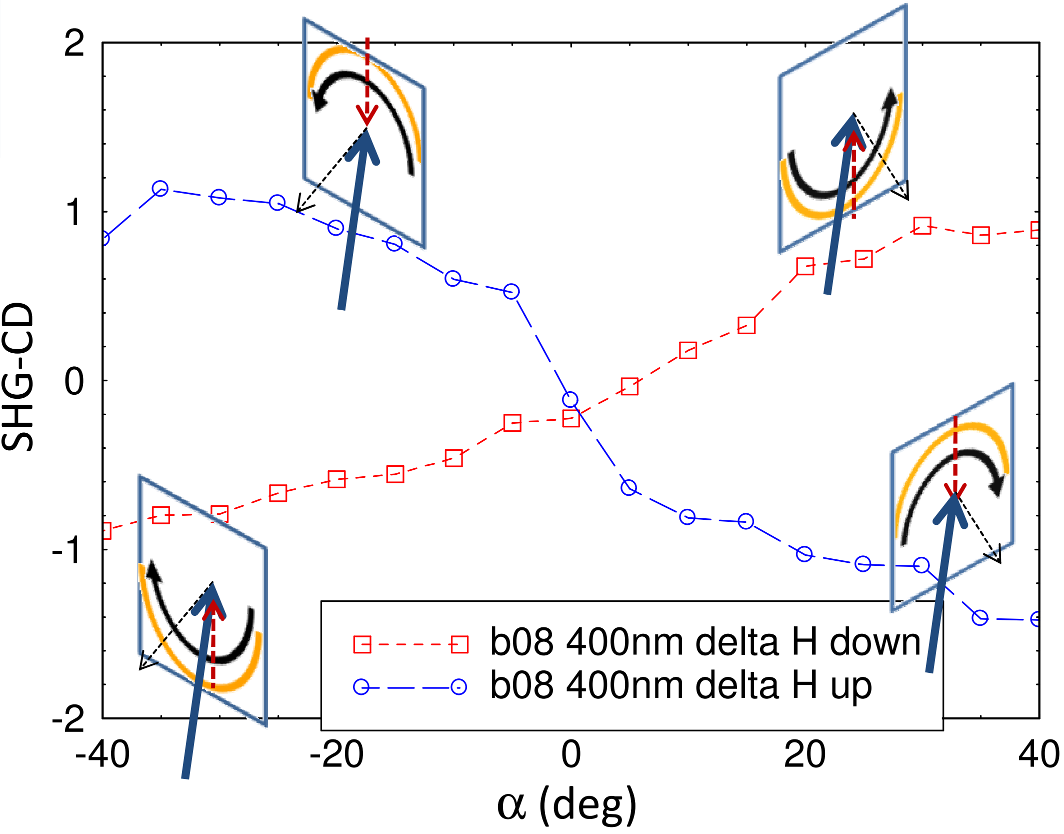
SHG measurements on sample B – P pol





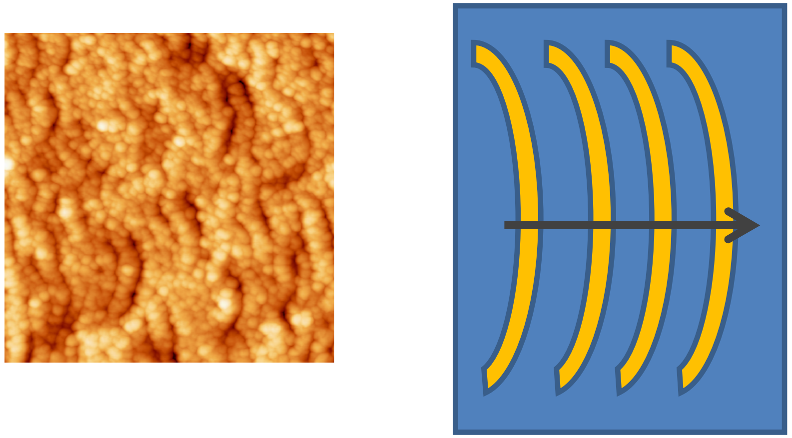
SHG measurements on sample A – P pol

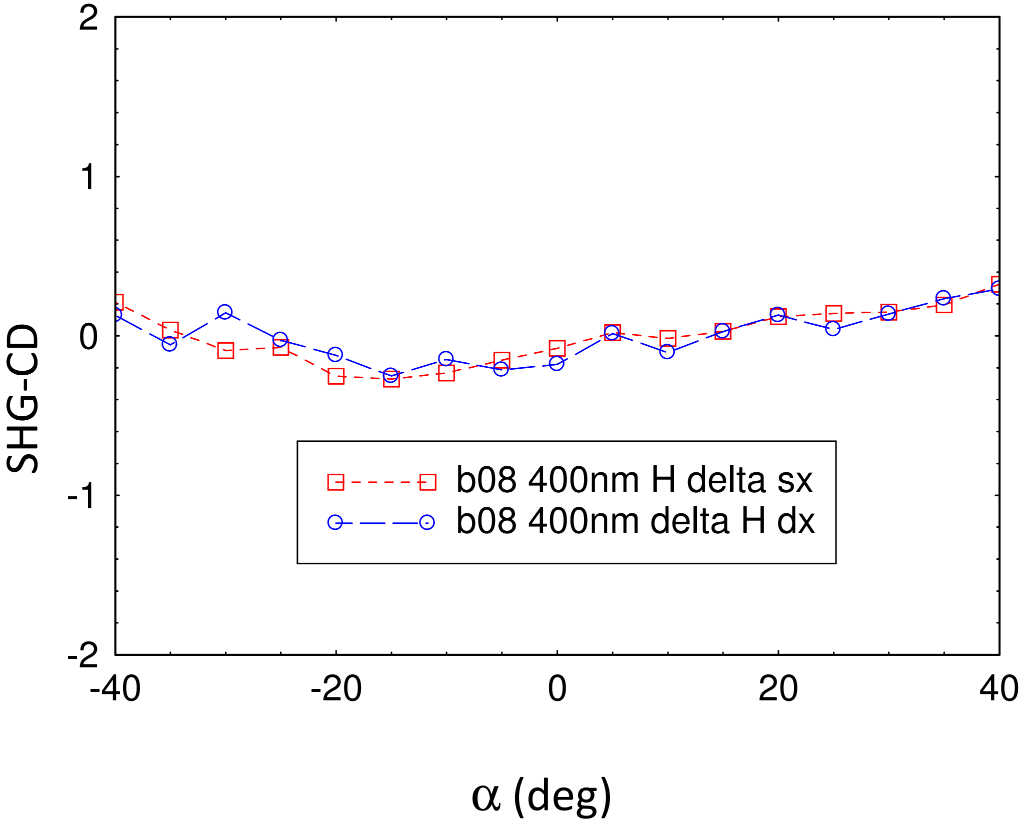


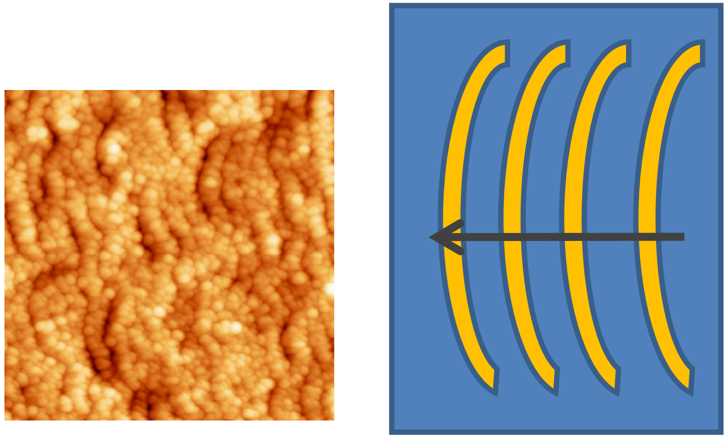


A.Belardini et al PRL
2011

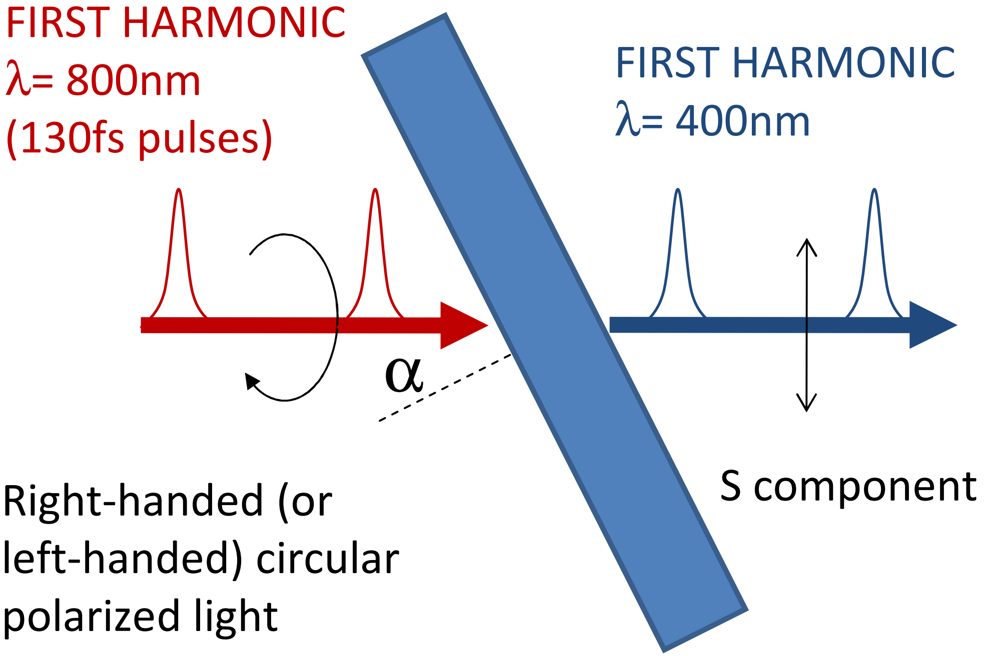
SHG measurements on sample A – P pol







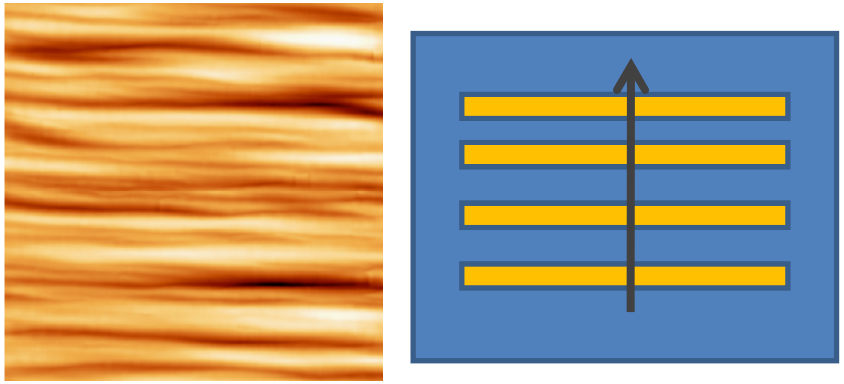
SHG measurements – S pol

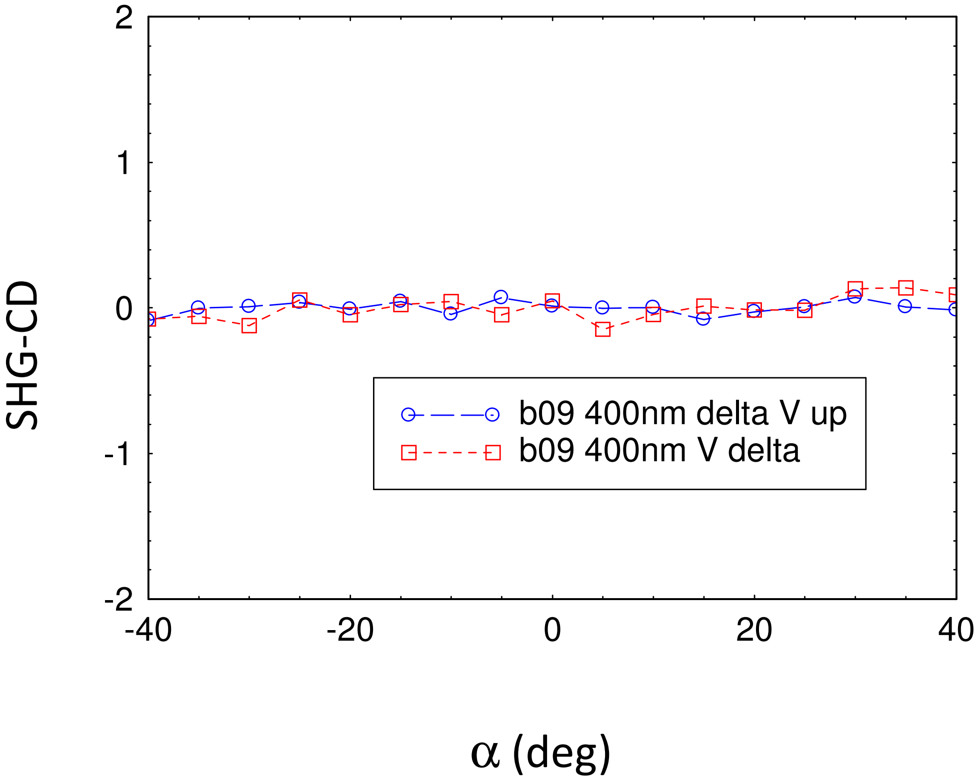


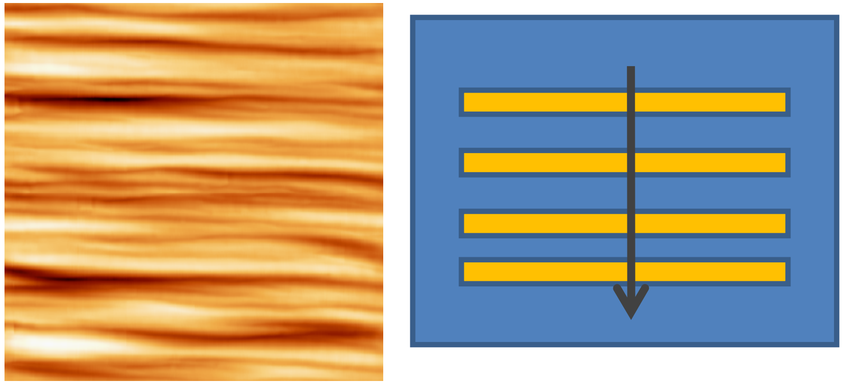
Second harmonic generation - circular dichroism (SHG-CD)

$$SHG-CD=\frac{I_L^{2\omega}-I_R^{2\omega}}{(I_L^{2\omega}+I_R^{2\omega})/2}$$

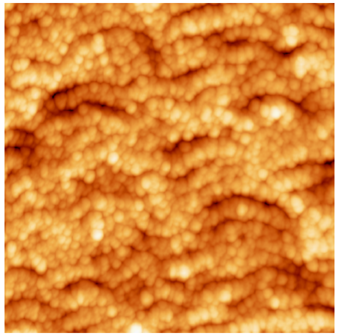
SHG measurements on sample B – S pol

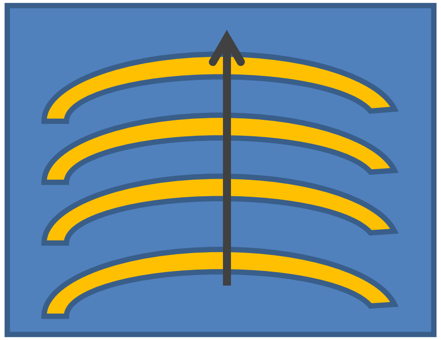


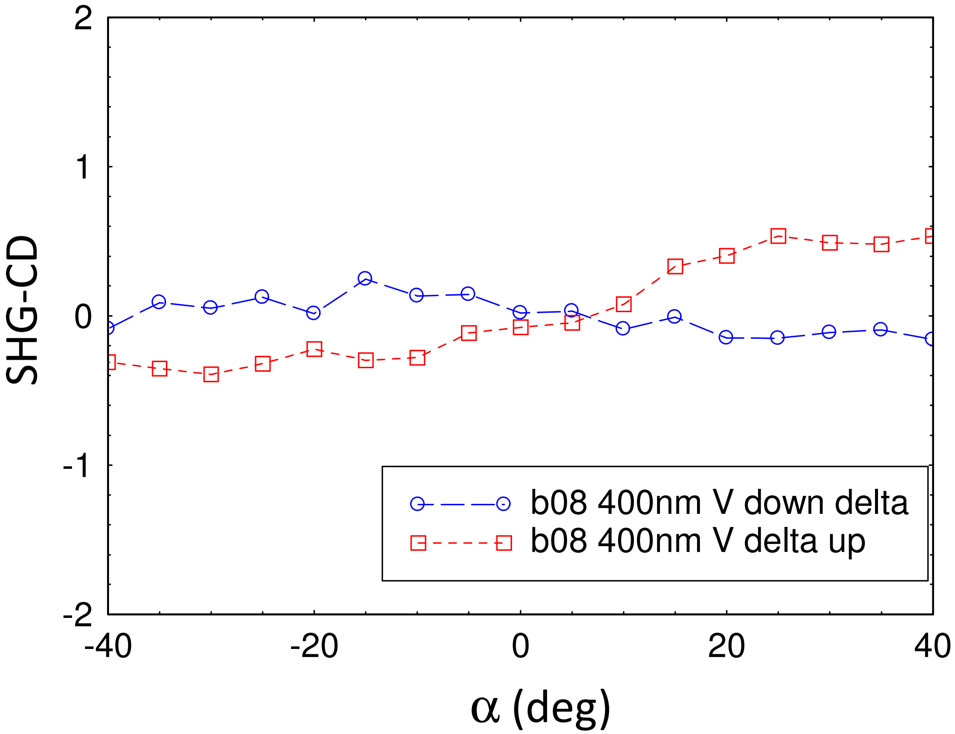


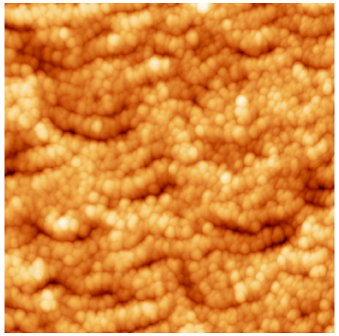


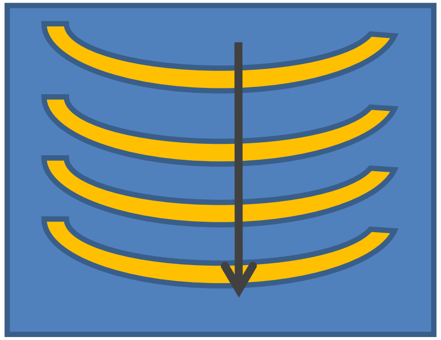
SHG measurements on sample A – S pol







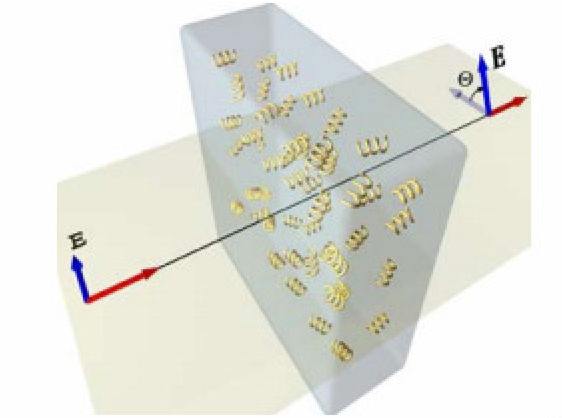


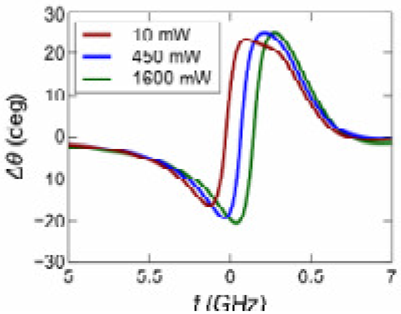


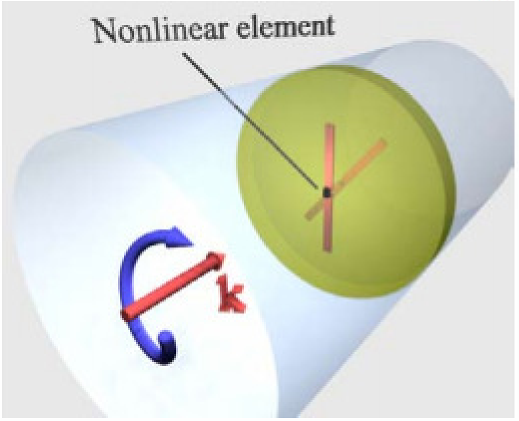
Chiral Metamaterials
Unlocking Nonlinear Optical Activity
Intensity dependent effects

AOS News Volume 25 Number 1 2011

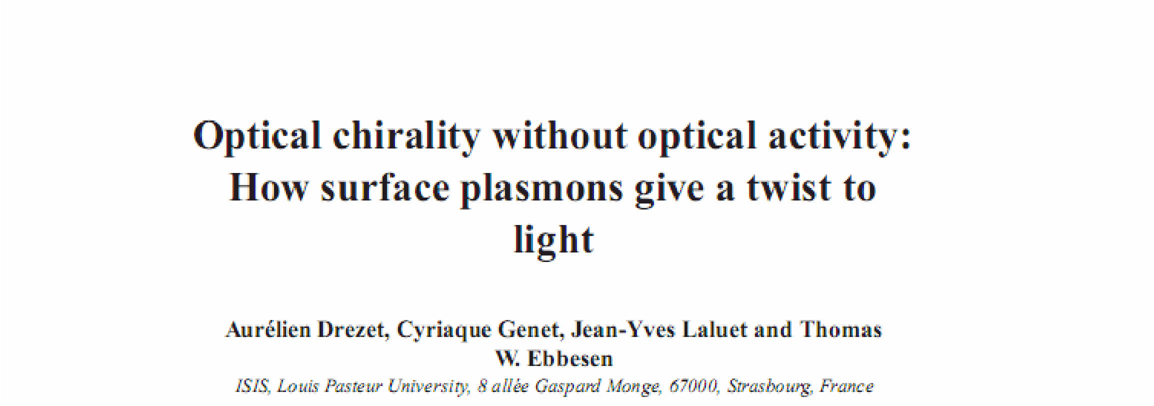
by David A. Powell, Ilya V. Shadrivov, Vassili A. Fedotov, Nikolay I. Zheludev and Yuri S. Kivshar





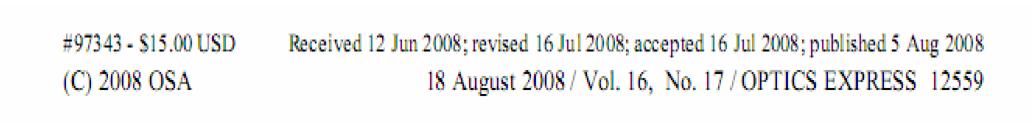


Optical diode for cicular polarized ligth



Optical chirality without optical activity: How surface plasmons give a twist to light

Aurélien Drezet, Cyriaque Genet, Jean-Yves Laluet and Thomas W. Ebbesen
ISIS, Louis Pasteur University, 8 allée Gaspard Monge, 67000, Strasbourg, France



#97343 - $15.00 USD Received 12 Jun 2008; revised 16 Jul 2008; accepted 16 Jul 2008; published 5 Aug 2008
(C) 2008 OSA 18 August 2008 / Vol. 16, No. 17 / OPTICS EXPRESS 12559

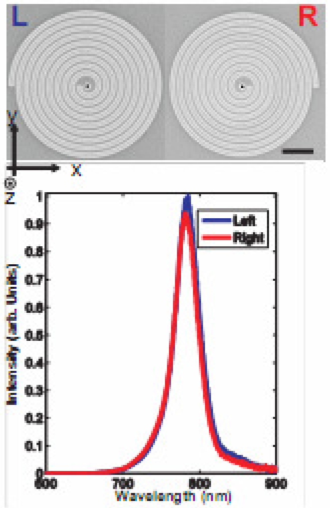


Fig. 1. Chiral plasmonic metamolecules. On the top panel: scanning electron micrographs of the left (L) and right (R) handed enantiomer (mirror image) planar chiral structures investigated. The scale bar is 3 μm long. The parameters characterizing the structure are the

- 3D, 2D-chirality, Extrinsic chirality
- SHG as chirality detection method
- Nonlinear measurements
- Intensity dependence

Acknwoledgments

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C.Gergeley – Univ. Montpellier2 – Montpellier-Fr
F.Buatier- University of Genova -Italy

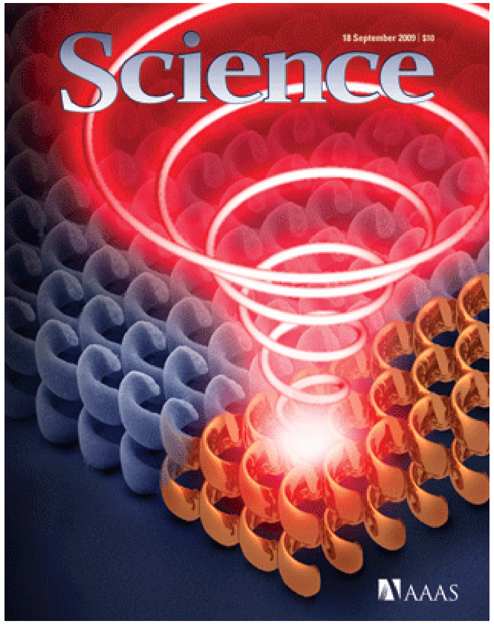
Thank you !!!

SAPIENZA
UNIVERSITÀ DI ROMA

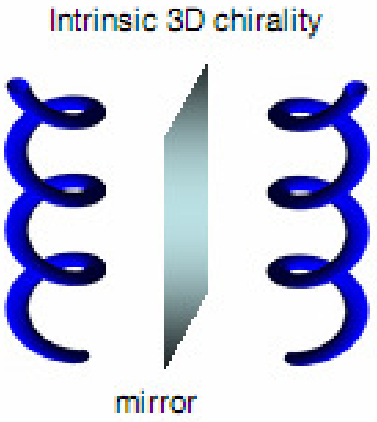
Nonlinear Optics of chiral materials

Concita Sibilia
Dipartimento SBAI-Universita’ di Roma La Sapienza

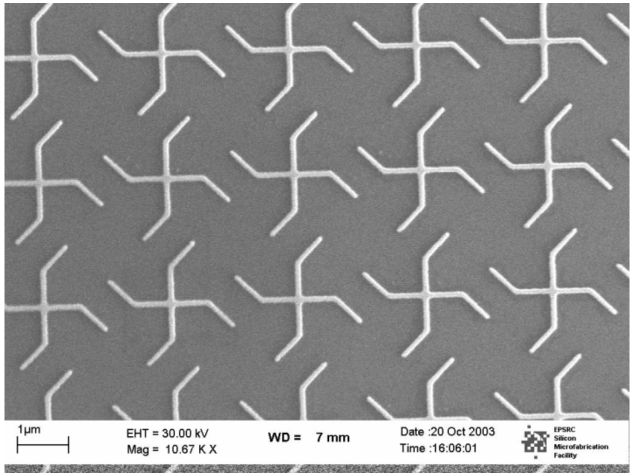
3D and 2D Chirality



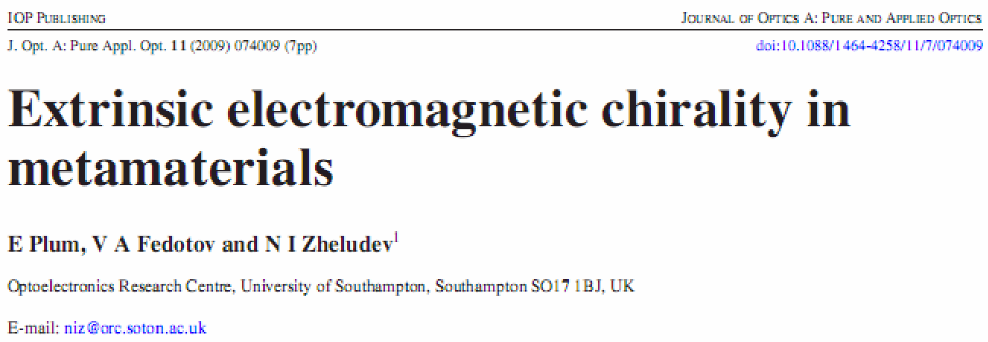
3D chiral metamaterial



Absence of mirror rotation axis



2D chiral metamaterial



IOP PUBLISHING — JOURNAL OF OPTICS A: PURE AND APPLIED OPTICS

J. Opt. A: Pure Appl. Opt. 11 (2009) 074009 (7pp) — doi:10.1088/1464-4258/11/7/074009

Extrinsic electromagnetic chirality in metamaterials

E Plum, V A Fedotov and N I Zheludev[1]

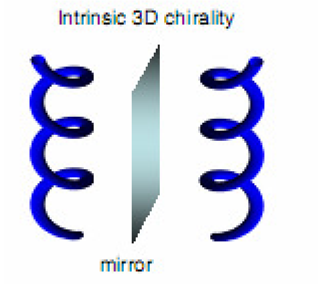
Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, UK

E-mail: niz@orc.soton.ac.uk

In the last years a lot of effort was devoted to the study on chiral metamaterials

Both 3D- and 2D-chiral metamaterials were studied

From N.Zheludev



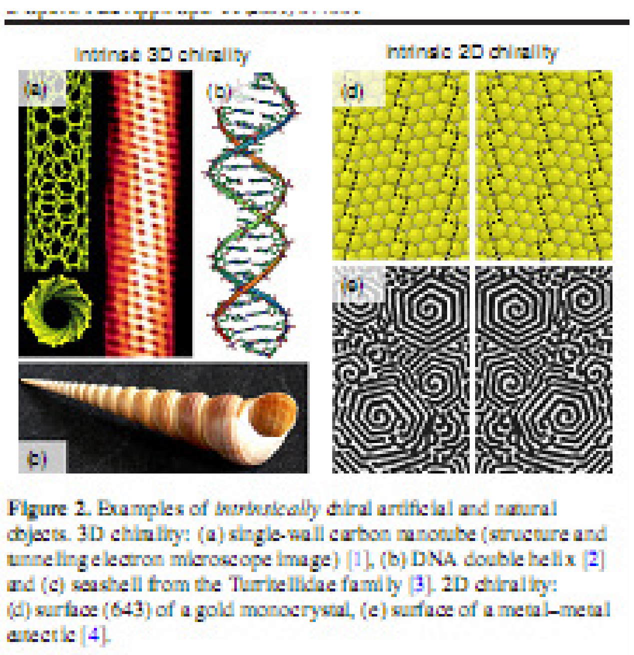
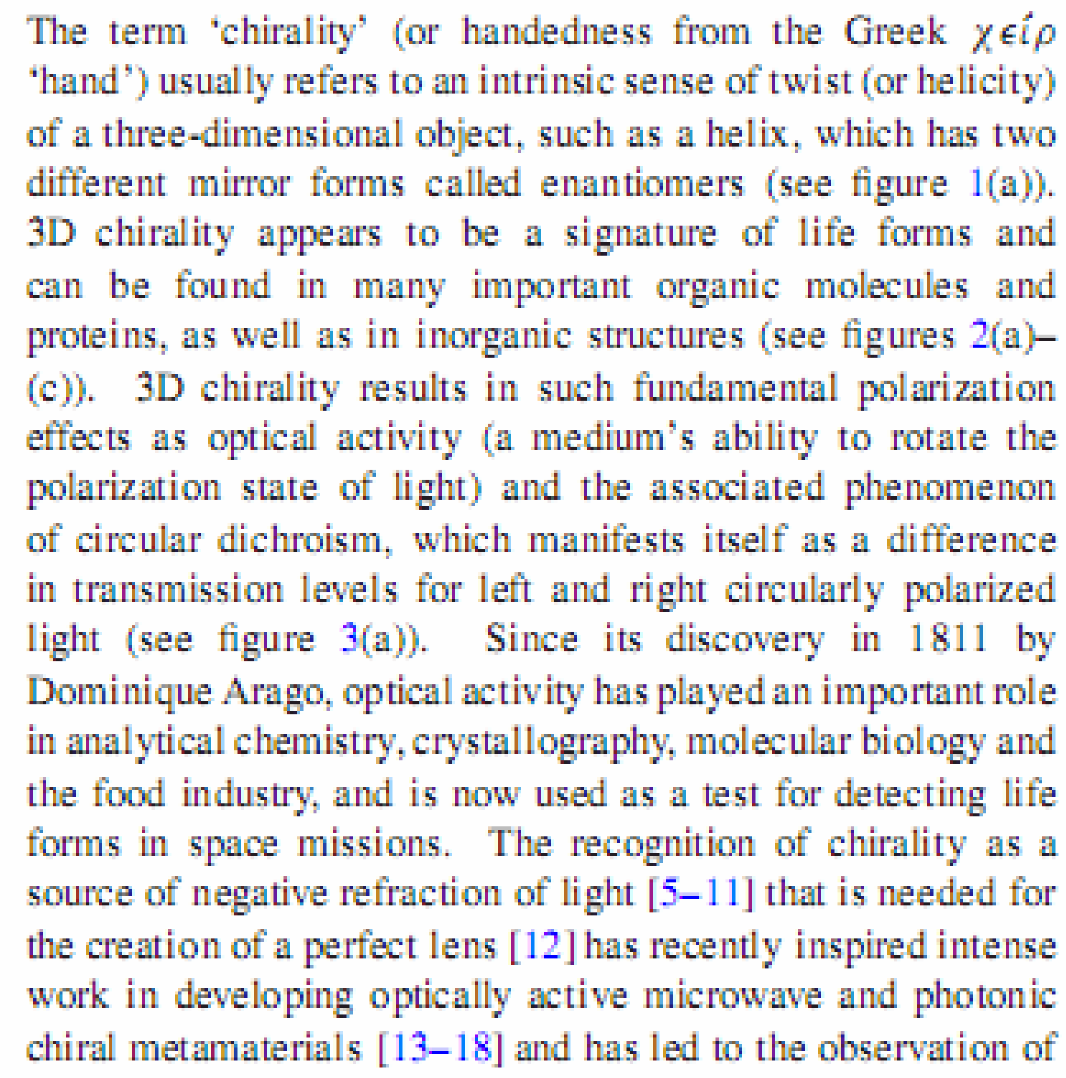


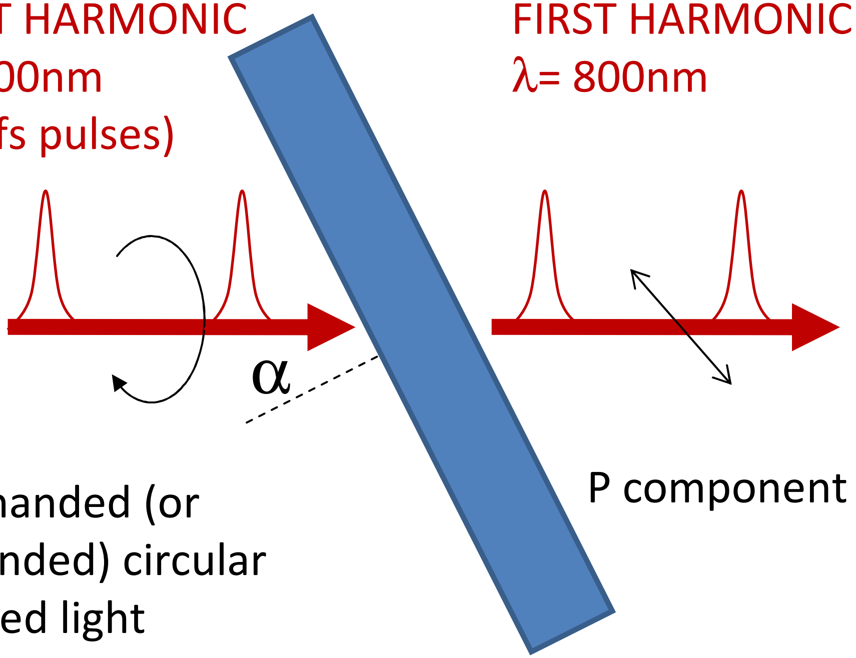
Figure 2. Examples of *intrinsically* chiral artificial and natural objects. 3D chirality: (a) single-wall carbon nanotube (structure and tunneling electron microscope image) [1], (b) DNA double helix [2] and (c) seashell from the Turritellidae family [3]. 2D chirality: (d) surface (643) of a gold monocrystal, (e) surface of a metal–metal eutectic [4].



The term 'chirality' (or handedness from the Greek $\chi\epsilon\acute{\iota}\rho$ 'hand') usually refers to an intrinsic sense of twist (or helicity) of a three-dimensional object, such as a helix, which has two different mirror forms called enantiomers (see figure 1(a)). 3D chirality appears to be a signature of life forms and can be found in many important organic molecules and proteins, as well as in inorganic structures (see figures 2(a)–(c)). 3D chirality results in such fundamental polarization effects as optical activity (a medium's ability to rotate the polarization state of light) and the associated phenomenon of circular dichroism, which manifests itself as a difference in transmission levels for left and right circularly polarized light (see figure 3(a)). Since its discovery in 1811 by Dominique Arago, optical activity has played an important role in analytical chemistry, crystallography, molecular biology and the food industry, and is now used as a test for detecting life forms in space missions. The recognition of chirality as a source of negative refraction of light [5–11] that is needed for the creation of a perfect lens [12] has recently inspired intense work in developing optically active microwave and photonic chiral metamaterials [13–18] and has led to the observation of

Linear measurements

The measurements performed as a function of the incidence angle α



FIRST HARMONIC
λ= 800nm
(130fs pulses)

FIRST HARMONIC
λ= 800nm

Right-handed (or left-handed) circular polarized light

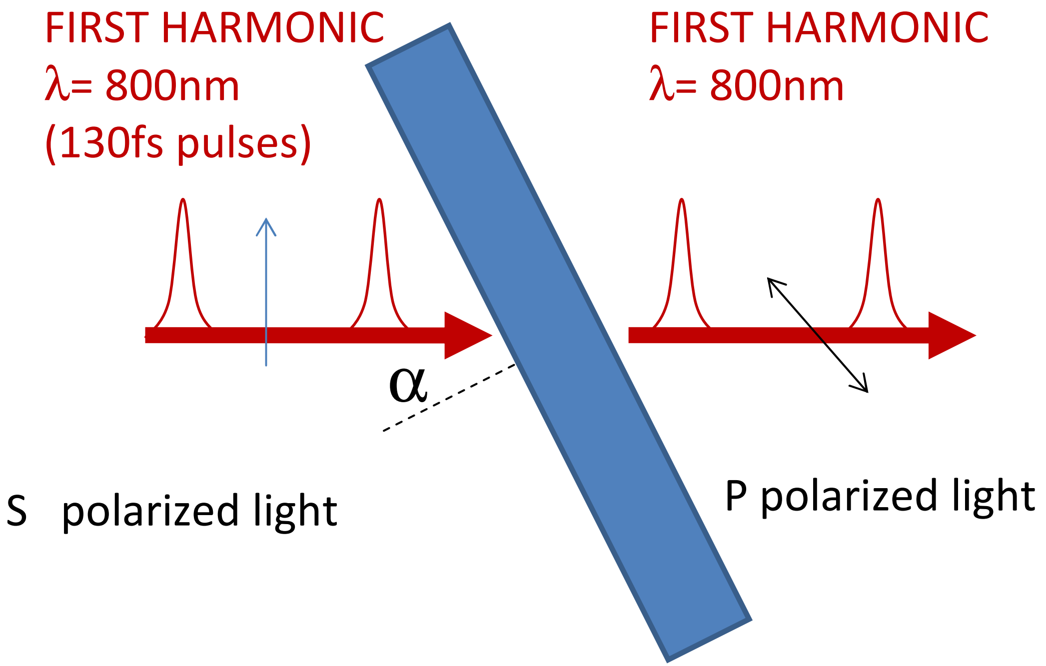
P component

circular dichroism (CD)

$$CD = \frac{I_L^{\omega} - I_R^{\omega}}{(I_L^{\omega} + I_R^{\omega})/2}$$

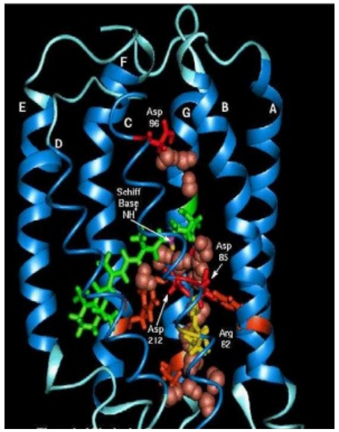
Linear measurements

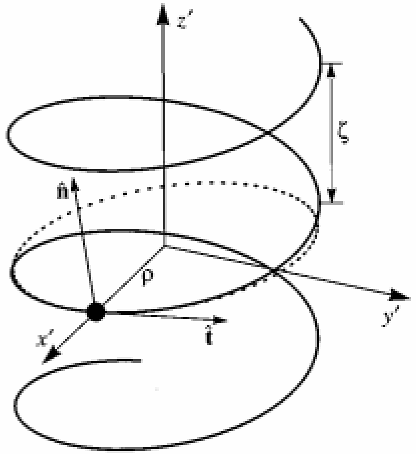
The measurements performed as a function of the incidence angle α



ORD - Rotation dispersion

As the electrons of chiral molecules are displaced from their equilibrium by the application of the electromagnetic field, they are forced helical like paths





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

weak

Nonlinear optics, chirality, magneto-optics: a serendipitous road [Invited]

Andre Persoons[1,2,3,*]
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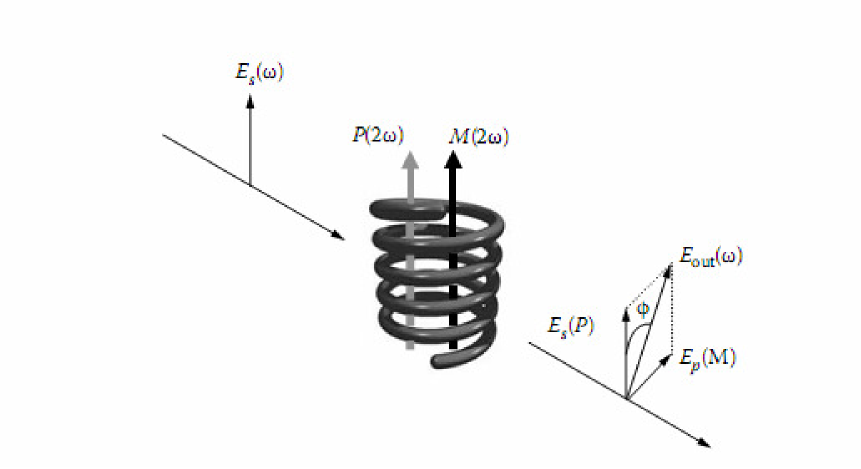
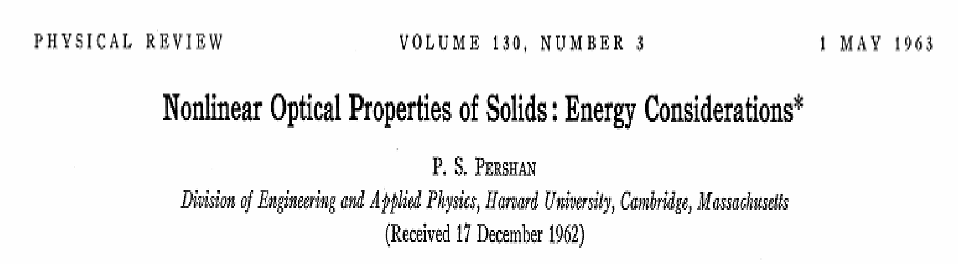
(C) 2011 OSA 1 May 2011 / Vol. 1, No. 1 / OPTICAL MATERIALS EXPRESS 5

Nonlinear Optical Activity



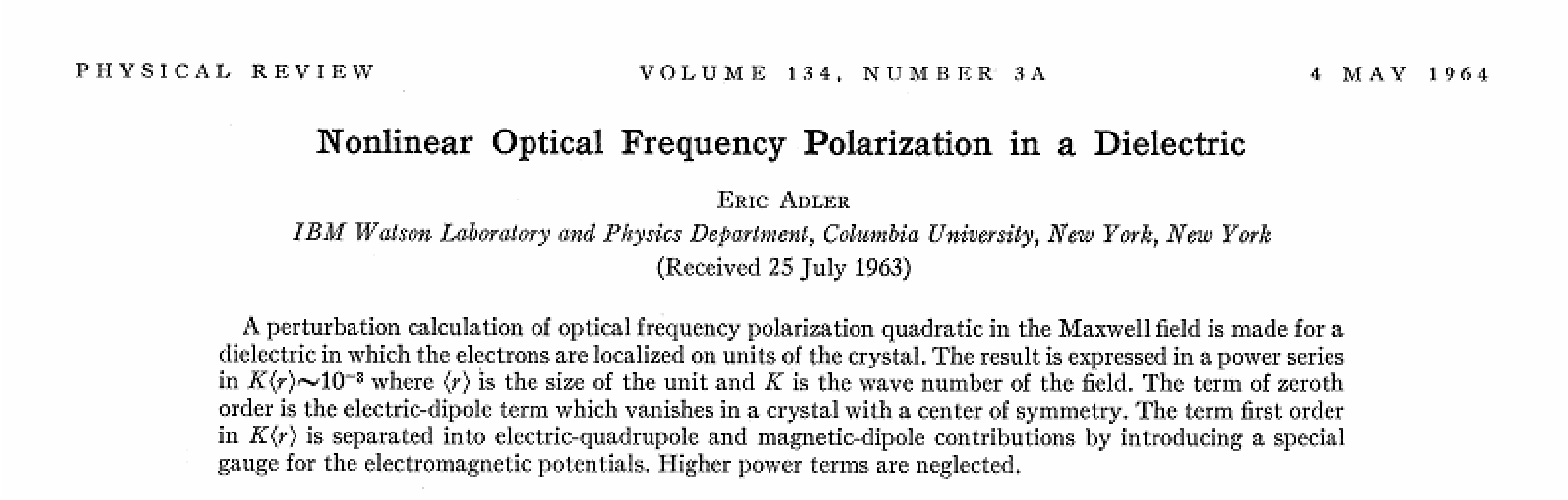
$$\chi^{(2)}_{IJK} = N\sum_{ijk}\langle (I\cdot i)(J\cdot j)(K\cdot k)\rangle \beta_{ijk}$$



PHYSICAL REVIEW VOLUME 130, NUMBER 3 1 MAY 1963

Nonlinear Optical Properties of Solids: Energy Considerations*

P. S. PERSHAN
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts
(Received 17 December 1962)



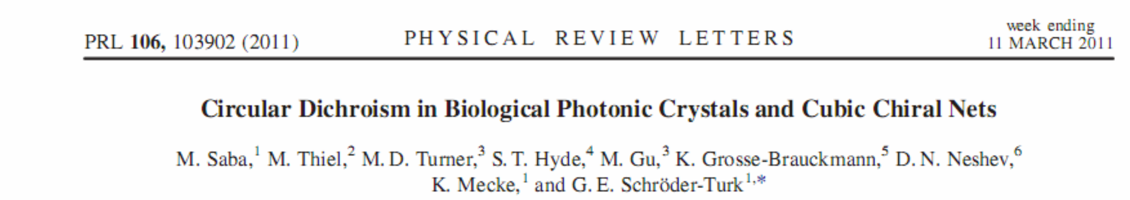
PHYSICAL REVIEW VOLUME 134, NUMBER 3A 4 MAY 1964

Nonlinear Optical Frequency Polarization in a Dielectric

ERIC ADLER
IBM Watson Laboratory and Physics Department, Columbia University, New York, New York

(Received 25 July 1963)

A perturbation calculation of optical frequency polarization quadratic in the Maxwell field is made for a dielectric in which the electrons are localized on units of the crystal. The result is expressed in a power series in $K\langle r\rangle \sim 10^{-8}$ where $\langle r\rangle$ is the size of the unit and K is the wave number of the field. The term of zeroth order is the electric-dipole term which vanishes in a crystal with a center of symmetry. The term first order in $K\langle r\rangle$ is separated into electric-quadrupole and magnetic-dipole contributions by introducing a special gauge for the electromagnetic potentials. Higher power terms are neglected.



PRL **106,** 103902 (2011) PHYSICAL REVIEW LETTERS week ending 11 MARCH 2011

Circular Dichroism in Biological Photonic Crystals and Cubic Chiral Nets

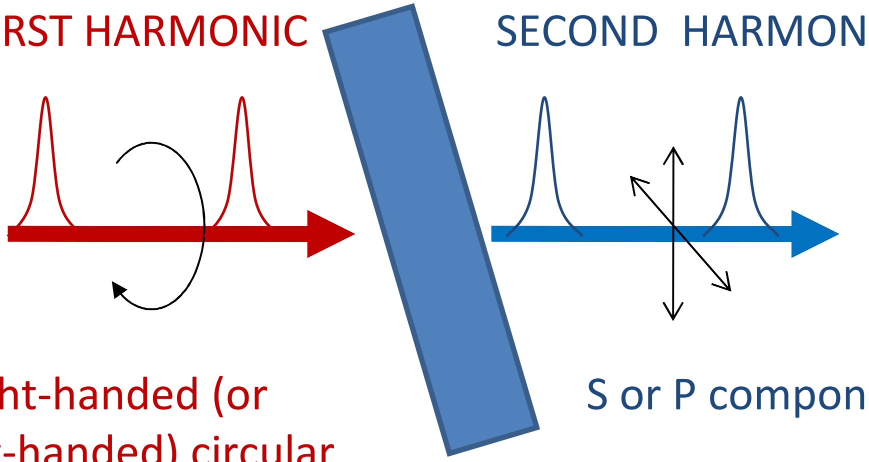
M. Saba,[1] M. Thiel,[2] M. D. Turner,[3] S. T. Hyde,[4] M. Gu,[3] K. Grosse-Brauckmann,[5] D. N. Neshev,[6]
K. Mecke,[1] and G. E. Schröder-Turk[1,*]

Second-Order Nonlinear Optical Imaging of Chiral Crystals
David J. Kissick, DebbieWanapun, and Garth J. Simpson
Department of Chemistry, Purdue University,West Lafayette, Indiana 47907;

Annu. Rev. Anal. Chem. 2011. 4:419–37

SHG as chirality detector

It is possible to investigate chirality via second harmonic generation experiments



FIRST HARMONIC

SECOND HARMONIC

Right-handed (or left-handed) circular polarized light

S or P component

One useful parameter is:
Second harmonic generation-circular dichroism (SHG-CD)

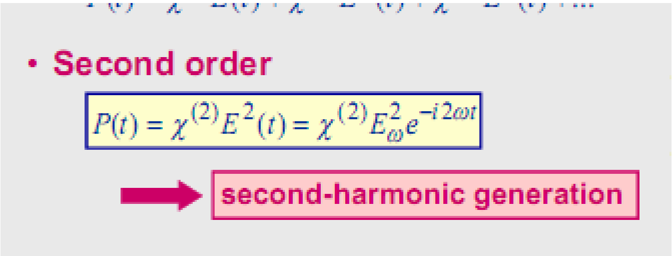
$$SHG - CD = \frac{I_L^{2\omega} - I_R^{2\omega}}{(I_L^{2\omega} + I_R^{2\omega})/2}$$

ORD

$$R(2\omega) = \frac{E_s(2\omega)}{E_p(2\omega)} = \frac{f_s E_p^2(\omega) + g_s E_s^2(\omega) + h_s E_p(\omega) E_s(\omega)}{f_p E_p^2(\omega) + g_p E_s^2(\omega) + h_p E_p(\omega) E_s(\omega)}$$

Verbiest, **Second-order Nonlinear Optical Characterization Techniques, Taylor & Francis (2009)**

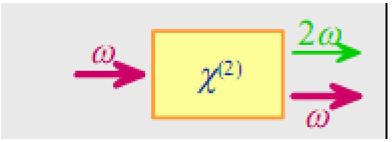
Intrinsic chirality



- Second order

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

→ second-harmonic generation



Multipolar Symmetries in SecondOrder Nonlinear Optics

– electric-dipole and higher-multipole nonlinearities –

-isotropic and centrosymmetric materials

Nonlinear susceptibility expansion

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

$$P(E) = \varepsilon_0\left(\chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \ldots\right)E$$

$$\vec{P}_{eff}(2\omega) = \vec{P}_D(2\omega) \; - \frac{1}{\omega}\vec{k}\; x\vec{M}(2\omega)$$

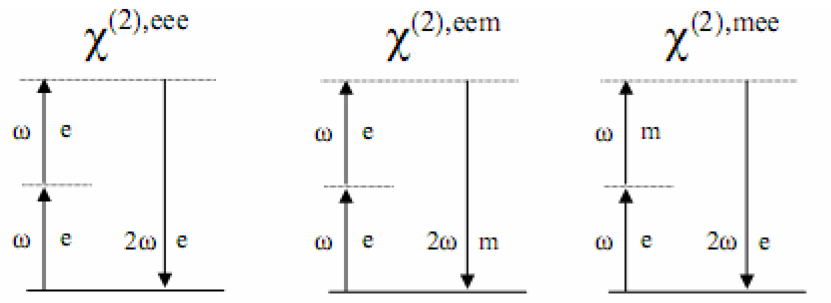
$$\vec{P}_D(2\omega) = \sum_{j,k} \chi_{ijk}^{(2)eee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{(2)eem} E_j(\omega) B_k(\omega)$$

Dipole dipole source

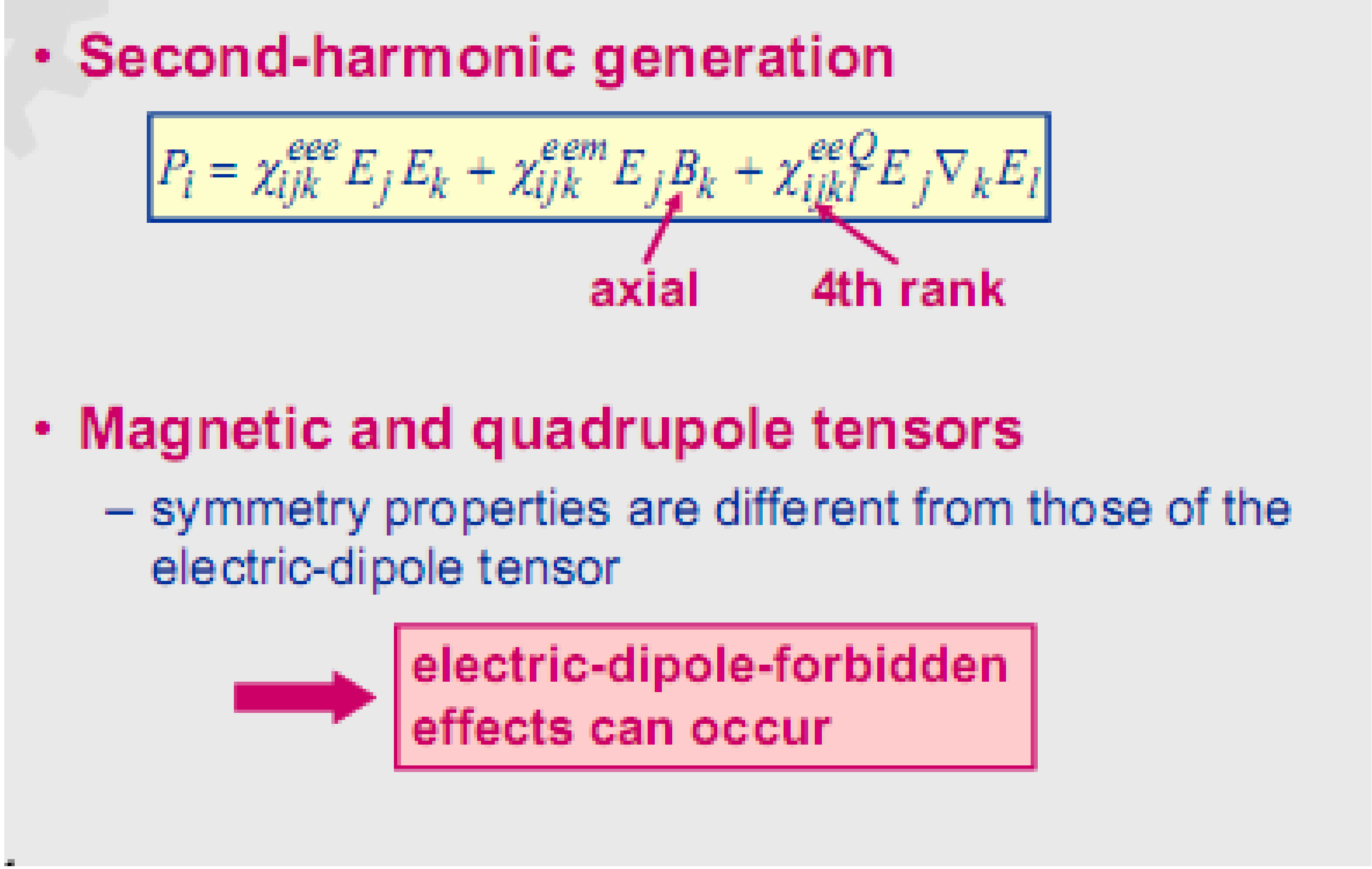
Magnetic dipole source

$$\vec{M}(2\omega) = \sum_{j,k} \chi_{ijk}^{(2)mee} E_j(\omega) E_k(\omega)$$

Nonlinear magnetization



Multipole symmetries



- **Second-harmonic generation**

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

axial 4th rank

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

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

χ(2) Nonlinear Interaction

bulk

Phase matching ==

$$\eta = \frac{P^{(2\omega)}(L)}{P^{(\omega)}(0)} \propto \sin c^2\left(\frac{1}{2}\Delta k L\right) \Rightarrow \underline{\Delta k = 0} \Longleftrightarrow \xcancel{n_o^{2\omega} < n_e^{\omega}}$$

equal PHASE velocity

For nonhogenous media- Phc

P.M. (equal PHASE velocity),

For SH $2K_1 = K_2$ ____ n(w) = n(2 w) ---if there is *geometrical dispersion*

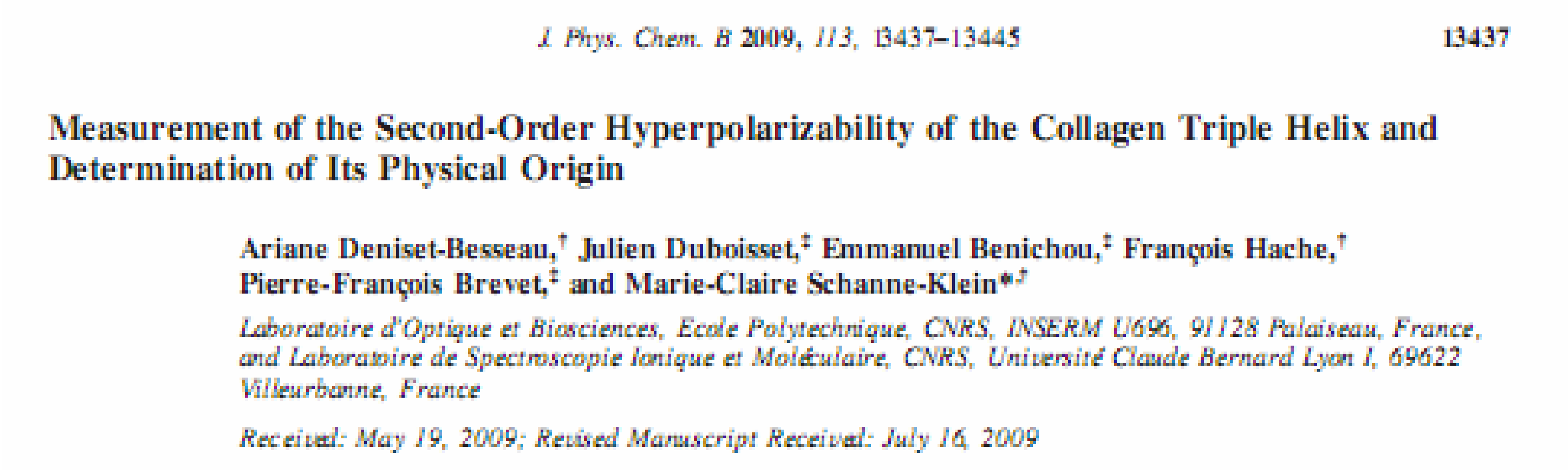
Thin films

No P.M. Interference between bound and free components (sourface and bulk)

At the nanoscale

No P.M. Field localization and overlap

materials



J. Phys. Chem. B 2009, 113, 13437–13445 13437

Measurement of the Second-Order Hyperpolarizability of the Collagen Triple Helix and Determination of Its Physical Origin

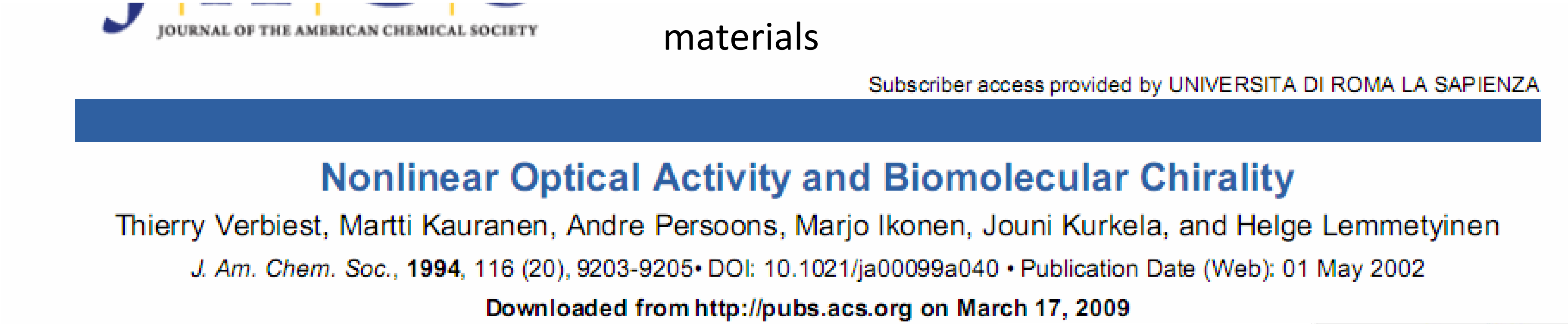
Ariane Deniset-Besseau,[†] Julien Duboisset,[‡] Emmanuel Benichou,[‡] François Hache,[†] Pierre-François Brevet,[‡] and Marie-Claire Schanne-Klein*[,†]

Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, INSERM U696, 91128 Palaiseau, France, and Laboratoire de Spectroscopie Ionique et Moléculaire, CNRS, Université Claude Bernard Lyon 1, 69622 Villeurbanne, France

Received: May 19, 2009; Revised Manuscript Received: July 16, 2009

$$\chi^{(2)}_{IJK} = N\sum_{ijk}\langle (I\cdot i)(J\cdot j)(K\cdot k)\rangle \beta_{ijk}$$

materials


JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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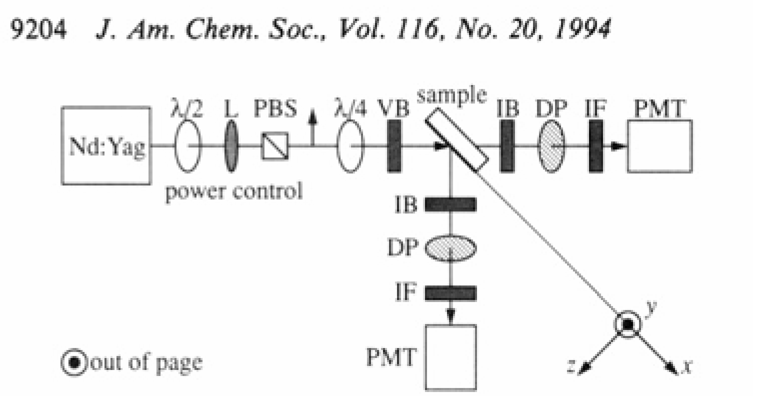
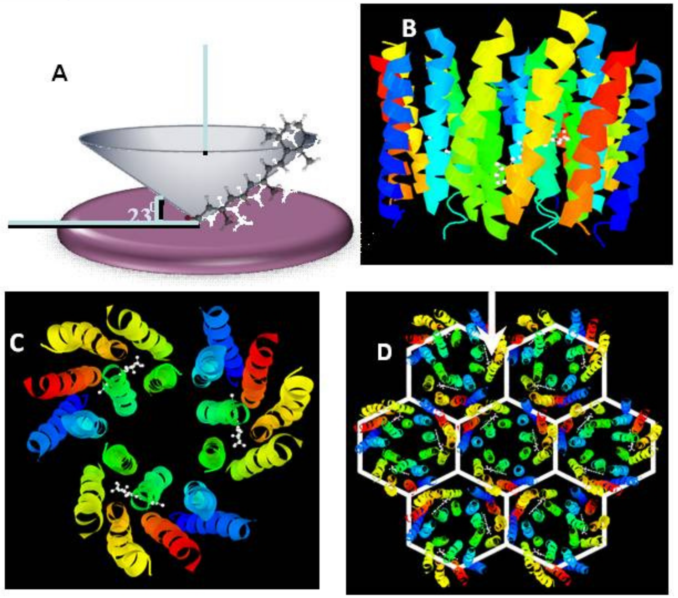
Nonlinear Optical Activity and Biomolecular Chirality

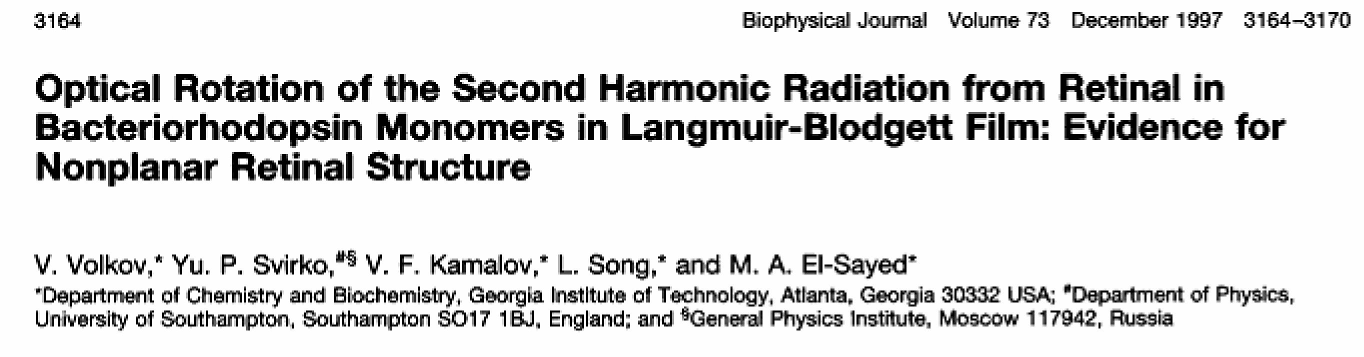
Thierry Verbiest, Martti Kauranen, Andre Persoons, Marjo Ikonen, Jouni Kurkela, and Helge Lemmetyinen

J. Am. Chem. Soc., **1994**, 116 (20), 9203-9205• DOI: 10.1021/ja00099a040 • Publication Date (Web): 01 May 2002

Downloaded from http://pubs.acs.org on March 17, 2009


9204 *J. Am. Chem. Soc., Vol. 116, No. 20, 1994*



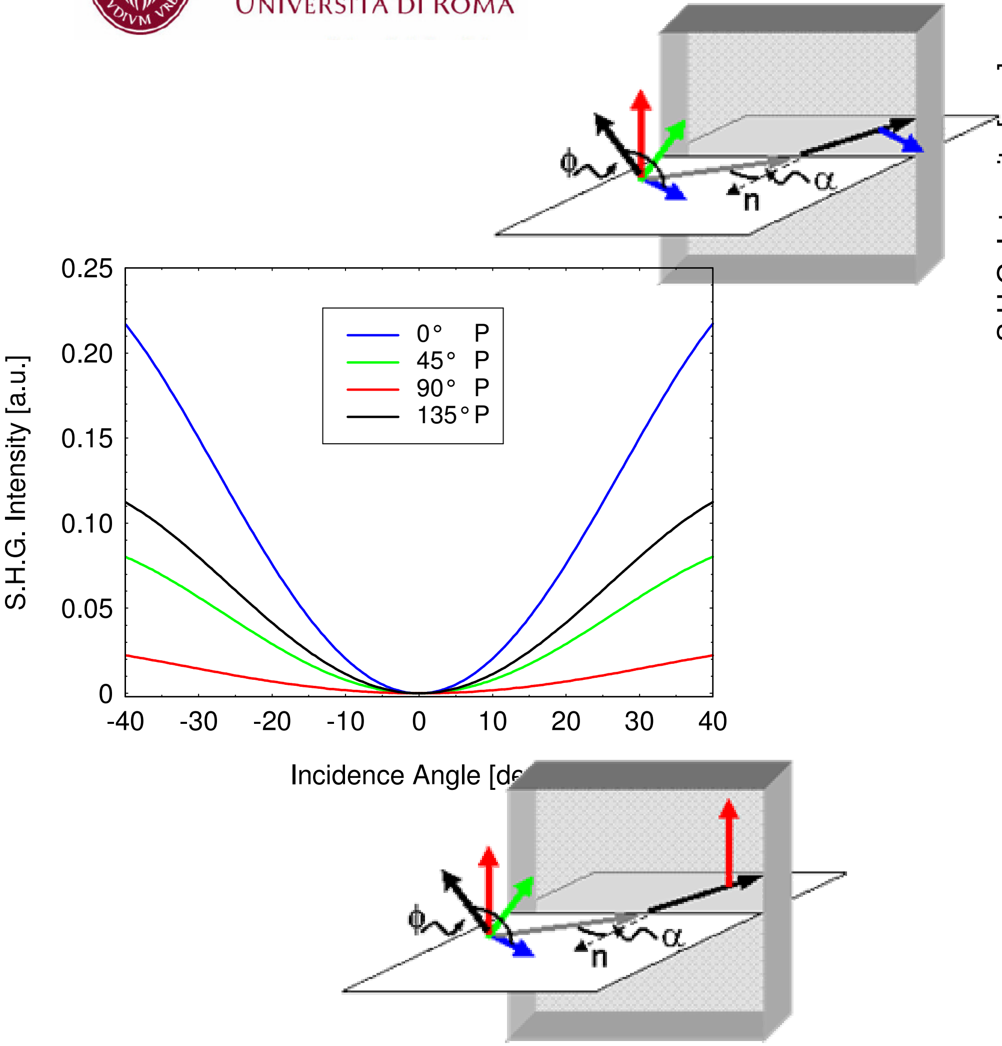

3164 Biophysical Journal Volume 73 December 1997 3164–3170

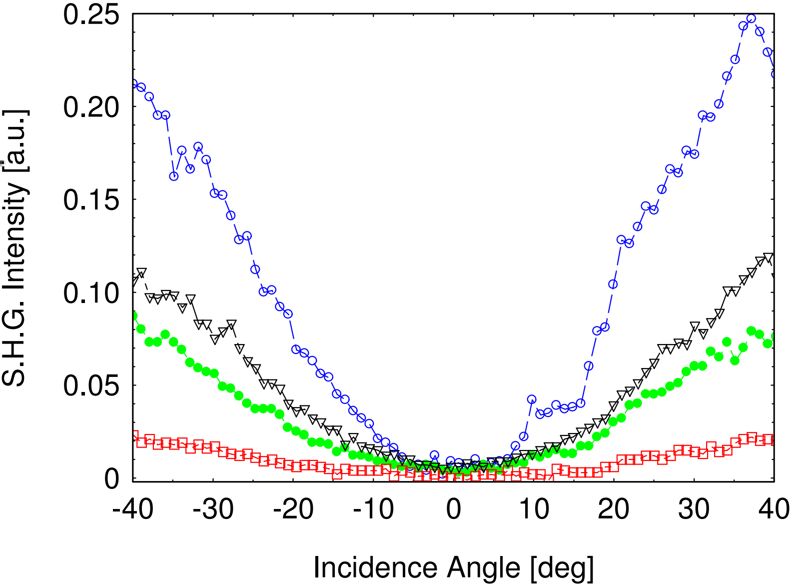
Optical Rotation of the Second Harmonic Radiation from Retinal in Bacteriorhodopsin Monomers in Langmuir-Blodgett Film: Evidence for Nonplanar Retinal Structure

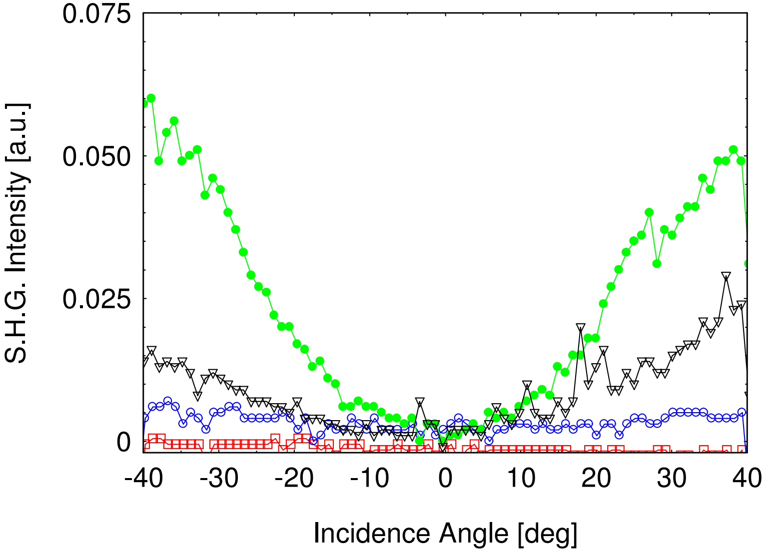
V. Volkov,* Yu. P. Svirko,#§ V. F. Kamalov,* L. Song,* and M. A. El-Sayed*

*Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 USA; #Department of Physics, University of Southampton, Southampton SO17 1BJ, England; and §General Physics Institute, Moscow 117942, Russia

Maker Fringes on BR



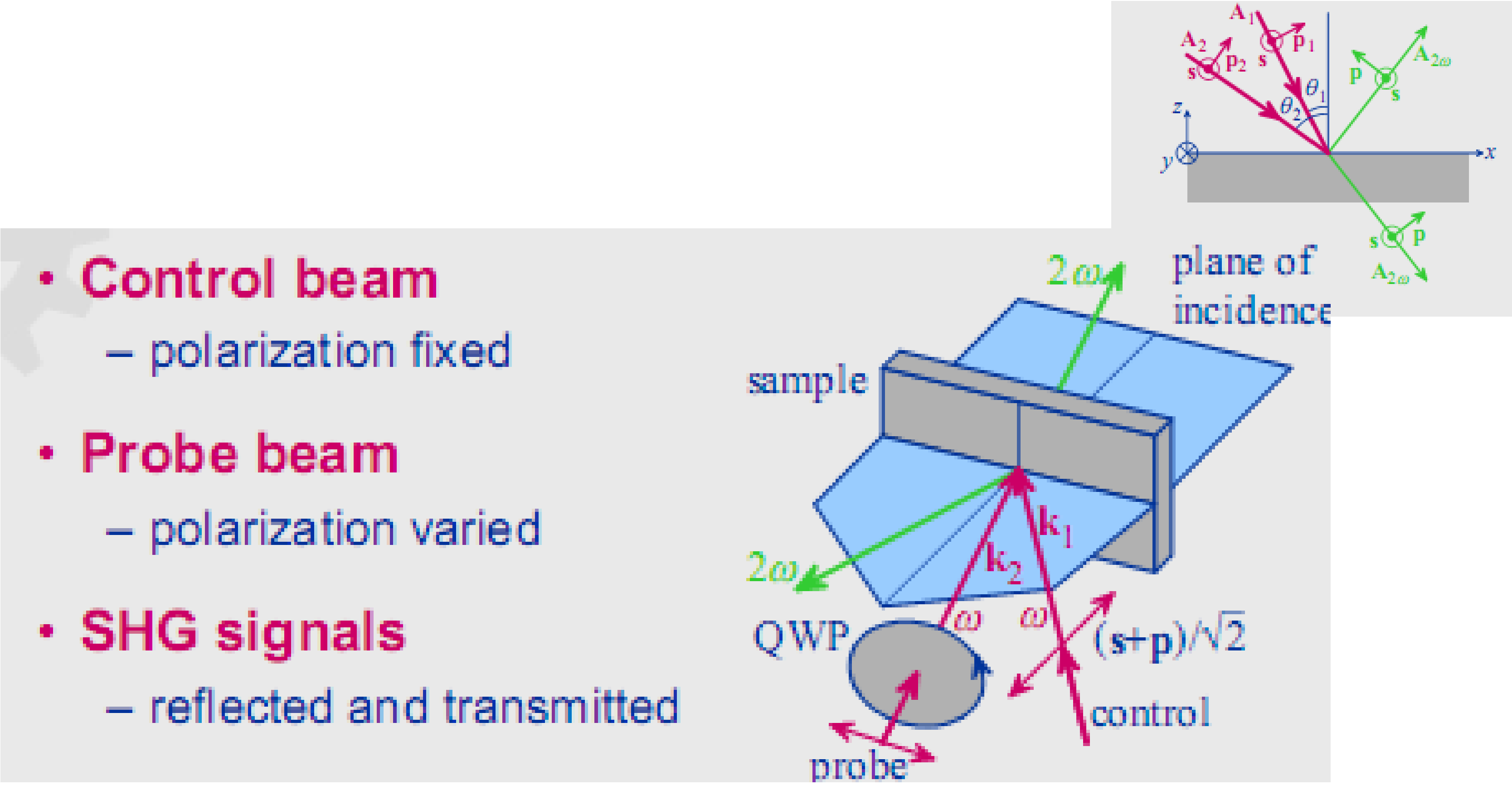




$d_{15}= d_{24}=$ 2.02 pm/V , $d_{31}= d_{32}=$ 2.44 pm/V , $d_{33}=$ 4.70 pm/V, as well as the chiral coefficients $d_{25}= - d_{14}=$ 0.34 pm/V.

M.Larciprete et al. APL 2009

Two beams



- **Control beam**
  - polarization fixed
- **Probe beam**
  - polarization varied
- **SHG signals**
  - reflected and transmitted

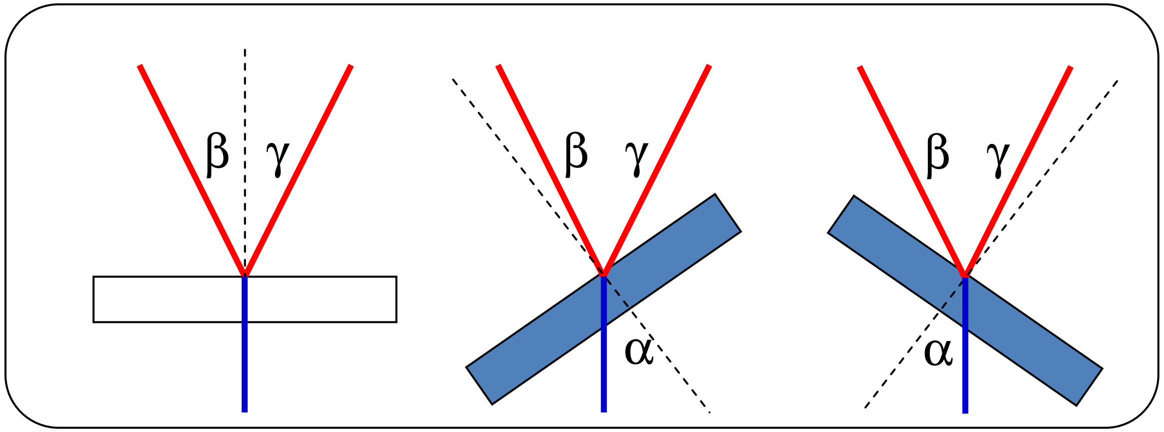
M.Kauranen et al
Progress in Optics

Second Harmonic Generation – Noncollinear case

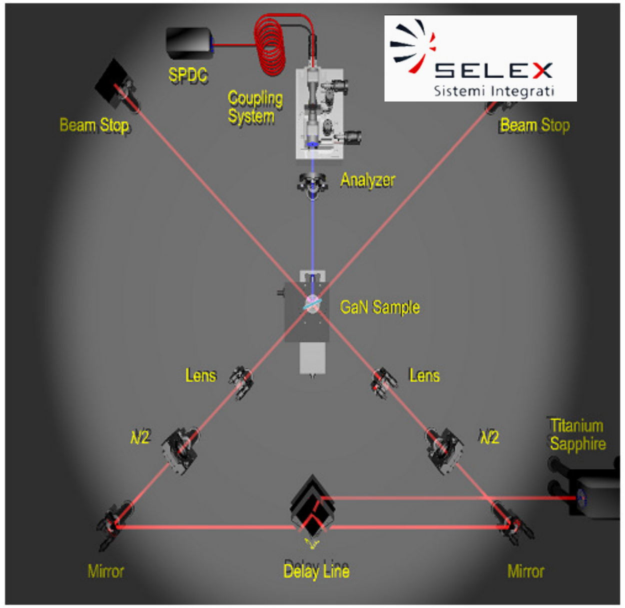
$$\mathbf{W}_{\omega1+\omega2}(\alpha)=\left(\frac{512\pi^3}{A}\right)\overbrace{(\mathbf{t}_{\omega1})^2\cdot(\mathbf{t}_{\omega2})^2}^{\text{Transmission Coefficient at }\omega\text{ for pump 1 \& 2}}\cdot\underset{\substack{\uparrow\\ \text{Transmittance at }2\omega}}{\mathbf{T}_{\omega1+\omega2}}\cdot\overbrace{\mathbf{W}_{\omega1}\cdot\mathbf{W}_{\omega2}}^{\text{Power of the field at }\omega\text{ for pump 1 \& 2}}\frac{\sin^2(\Psi_{SHG}(\alpha))}{\left[\mathbf{n}_{\omega1}\cdot\mathbf{n}_{\omega2}-\mathbf{n}^2_{\omega1+\omega2}\right]^2}(\mathbf{d}_{eff}(\alpha))^2$$

$$\Psi_{SHG}=\left(\frac{\pi L}{2}\right)\left(\frac{2}{\lambda}\right)\left[n_{\omega1}\cdot\cos(\alpha'_{\omega1})+n_{\omega2}\cdot\cos(\alpha'_{\omega2})-2n_{\omega1+\omega2}\cdot\cos(\alpha'_{\omega1+\omega2})\right]$$

- ✓ The difference between the two incidence angles is set to a fixed value (18°)



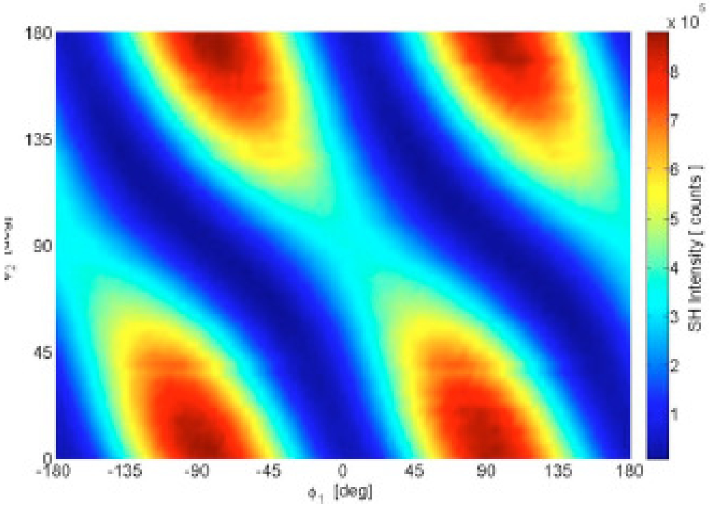
Polarization chart



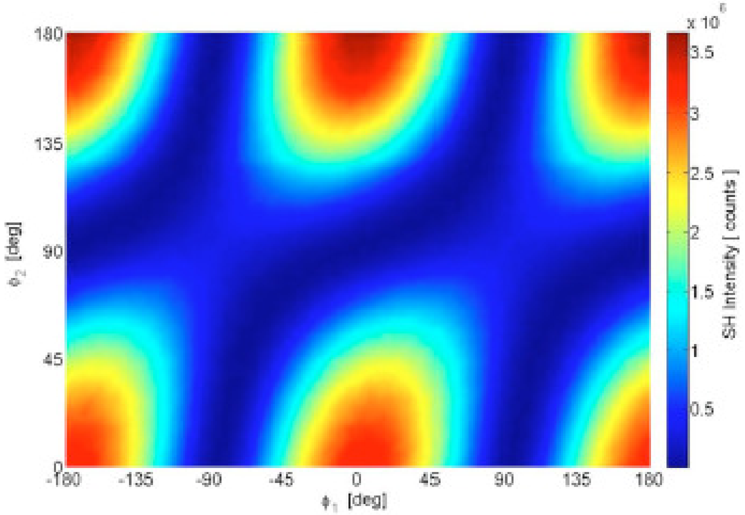
- At a fixed incidence angle, the generated signal is investigated by varying the polarization state of both fundamental beams.

- Example: GaN slab, ~300nm thick

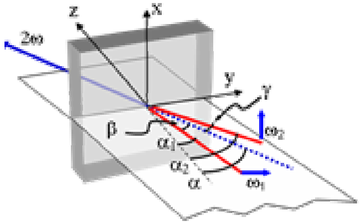
S-polarized SH signal



P-polarized SH signal

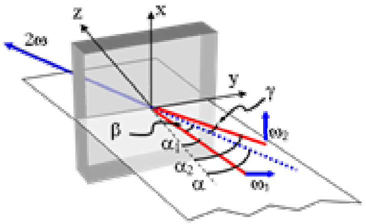


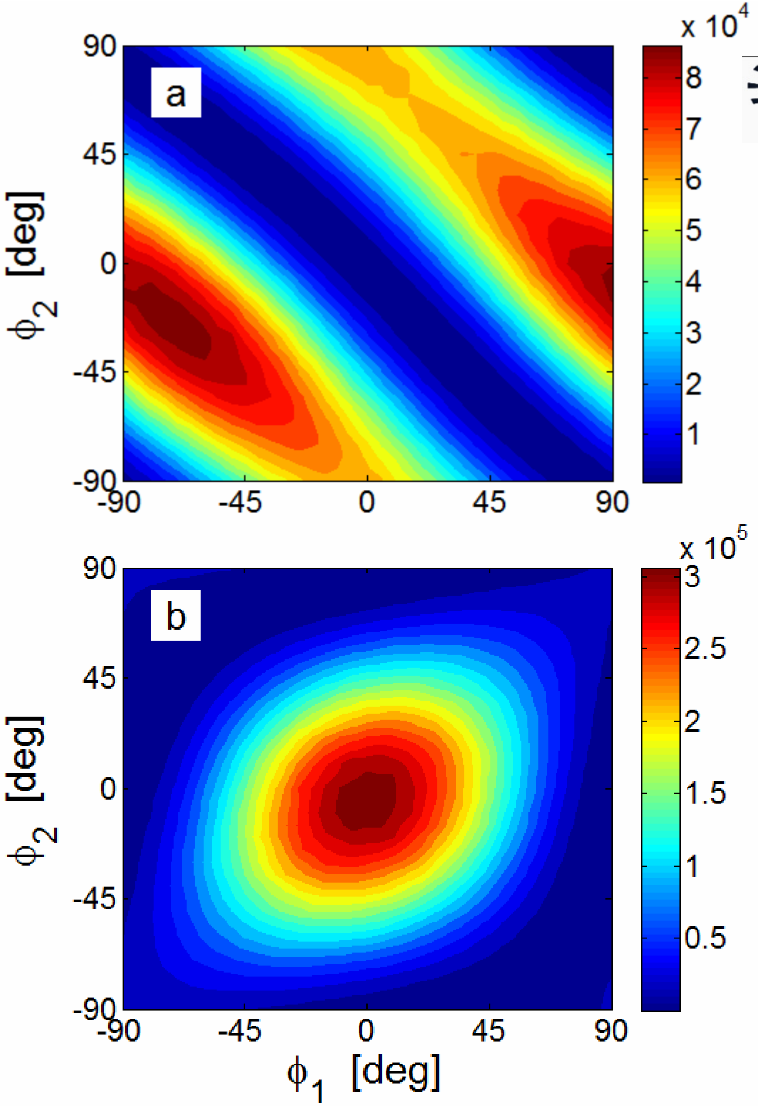
F.A.Bovino
Selex-SI-Genova

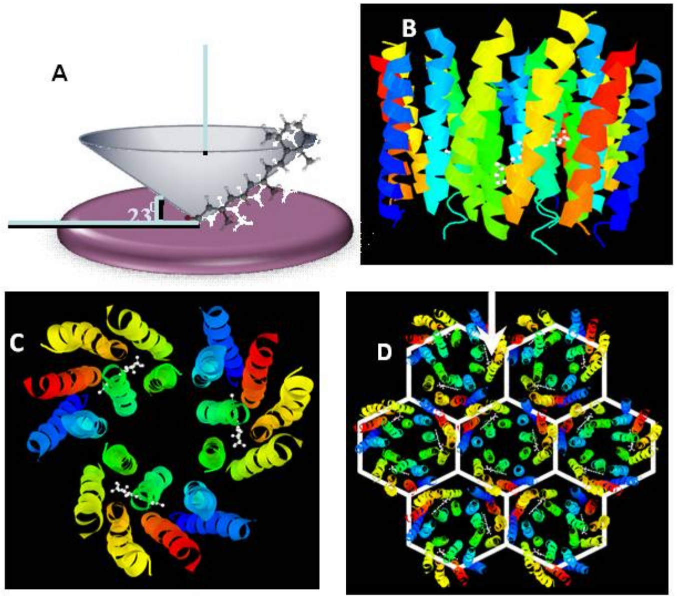


M.C.Larciprete,F.A.Bovino, M.Giardina, A.Belardini, M.Centini, C.Sibilia, M.Bertolotti, A. Passaseo and V.Tasco, "Mapping the nonlinear optical susceptibility by noncollinear second-harmonic generation", Optics Letters, Vol. 34, pp.2189-2191 (2009)

Polarization Chart in noncollinear SHG-BR







F.A Bovino et al- Selex-SI-Italy

Power of SH Signal

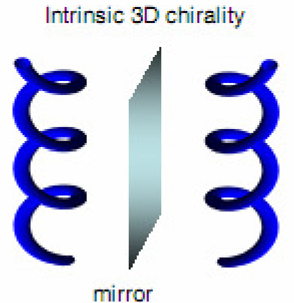
$$W_{\omega1+\omega2}(\alpha)=\left(\frac{512\pi^{3}}{A}\right)(t_{\omega1})^{2}\cdot(t_{\omega2})^{2}\cdot T_{\omega1+\omega2}\cdot W_{\omega1}\cdot W_{\omega2}\frac{\sin^{2}\left(\Psi_{SHG}(\alpha)\right)}{\left[n_{\omega1}\cdot n_{\omega2}-n^{2}_{\omega1+\omega2}\right]^{2}}\left(|d^{(2)}_{eff}(\alpha)|\right)^{2}$$

$$d^{(2)}_{eff}=\left(\hat{p}_{out}\right)\left(d_{il}{}^{(eee)}\right)(\hat{p}^{1\,e}_{in})(\hat{p}^{2\,e}_{in})+$$

$$\left(\hat{p}_{out}\right)\left(d_{il}{}^{(eem1)}\right)(\hat{p}^{1\,e}_{in})(\hat{p}^{2\,m}_{in})+\left(\hat{p}^{e}_{out}\right)\left(d_{il}{}^{(eem2)}\right)(\hat{p}^{1\,m}_{in})(\hat{p}^{2\,e}_{in})+$$

$$\left(\hat{p}_{out}\right)xK\left(d_{il}{}^{(mee)}\right)(\hat{p}^{1\,e}_{in})(\hat{p}^{2\,e}_{in})$$

$$d_{il}=\frac{\hat{\chi}_{ijk}^{(2)}}{2}$$



$\hat{p}_{out}$: *polarization versor of output sh signal*

$\hat{p}^{1}_{in}$: *polarization versor of input pump 1 signal*

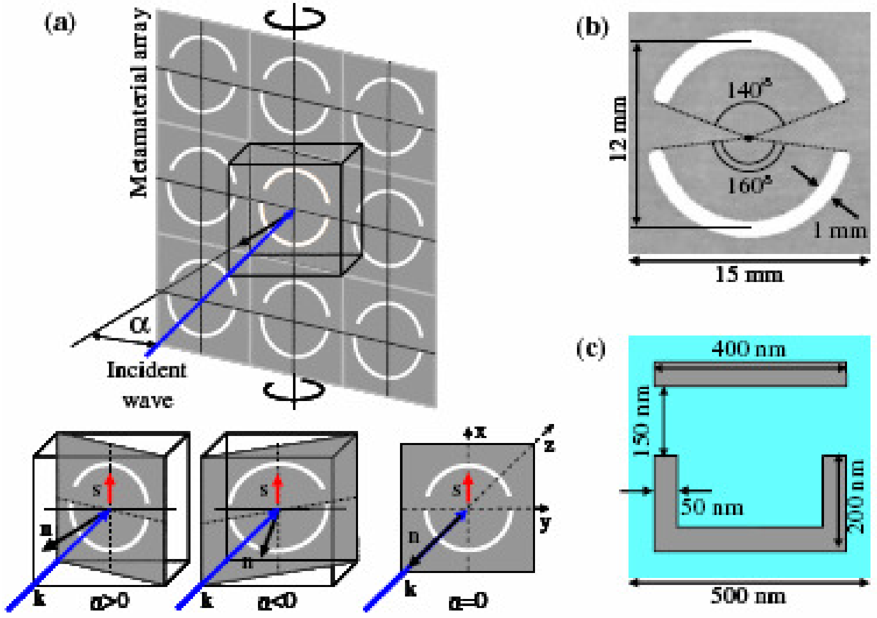
$\hat{p}^{2}_{in}$: *polarization versor of input pump 2 signal*

3p

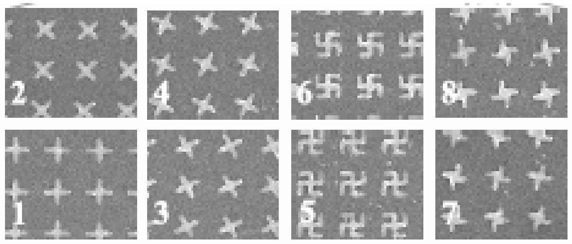
$$\begin{pmatrix}0&0&0&d_{14}^{eee}&d_{15}^{eee}&0\\0&0&0&d_{24}^{eee}&d_{25}^{eee}&0\\d_{31}^{eee}&d_{32}^{eee}&d_{33}^{eee}&0&0&0\end{pmatrix}\begin{pmatrix}0&0&0&d_{14}^{eem}&d_{15}^{eem}&0\\0&0&0&d_{24}^{eem}&d_{25}^{eem}&0\\d_{31}^{eem}&d_{32}^{eem}&d_{33}^{eem}&0&0&d_{36}^{eem}\end{pmatrix}\begin{pmatrix}0&0&0&d_{14}^{mee}&d_{15}^{mee}&0\\0&0&0&d_{24}^{mee}&d_{25}^{mee}&0\\d_{31}^{mee}&d_{32}^{mee}&d_{33}^{mee}&0&0&\end{pmatrix}$$

Extrinsic Chirality

E. Plum, PRL 102,113902 (2009)

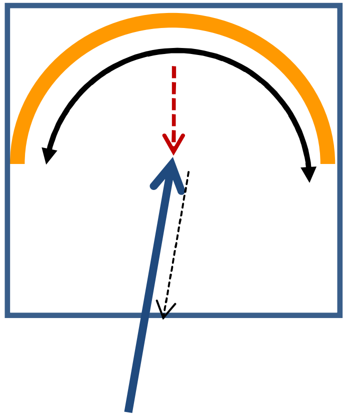


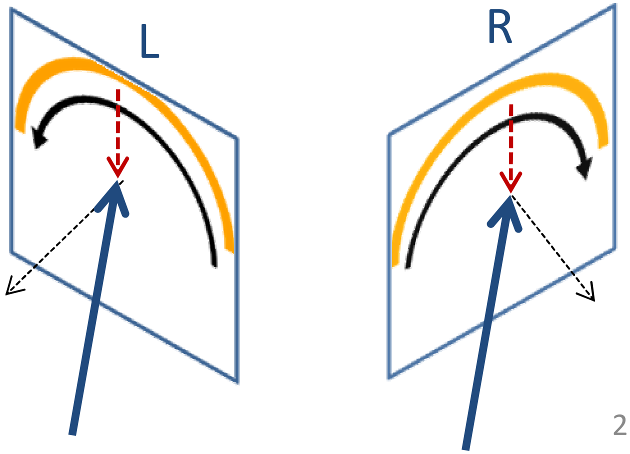
S.N. Volkov, PRA 79, 043819 (2009)



Extrinsic chirality: A non-chiral element breaks the symmetry when is tilted with respect the incidence light. The element thus assumes a chiral behavior

no-chirality

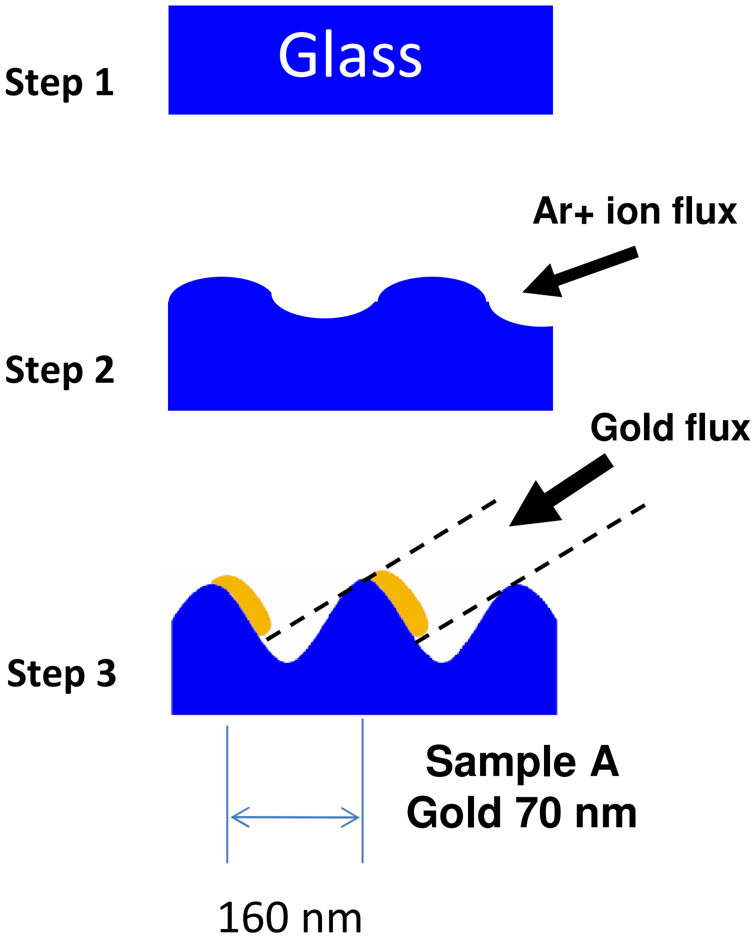




Extrinsic Chirality

Test sample fabrication – Sample A

Low cost self assembling procedure



Step 1

Glass

Step 2

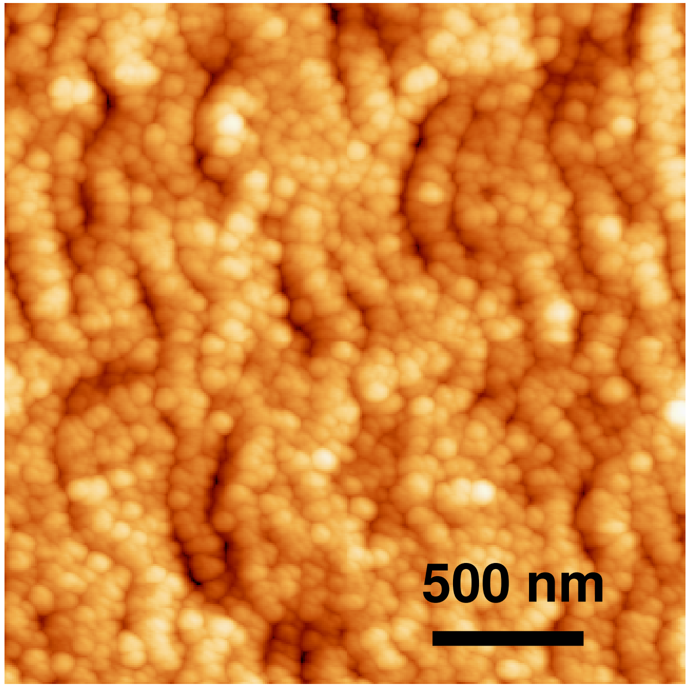
Ar+ ion flux

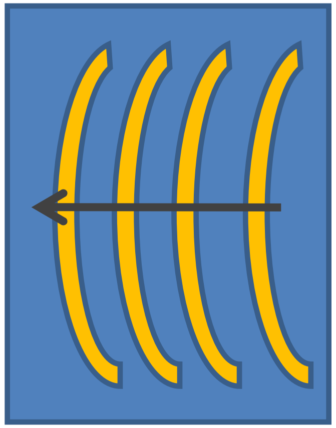
Gold flux

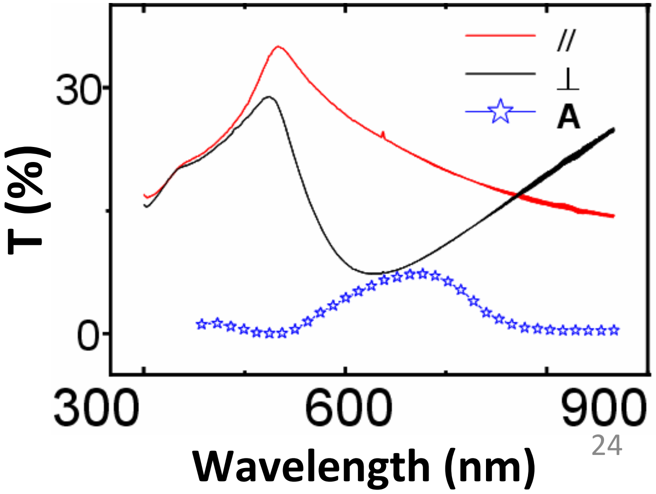
Step 3

Sample A
Gold 70 nm

160 nm

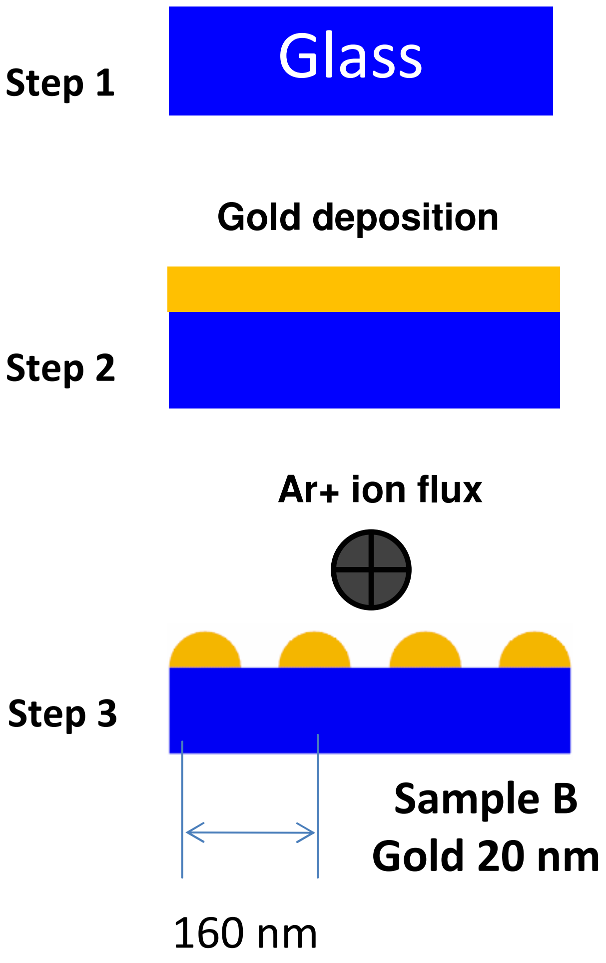






Reference sample fabrication – Sample B

Low cost self assembling procedure



Step 1

Glass

Gold deposition

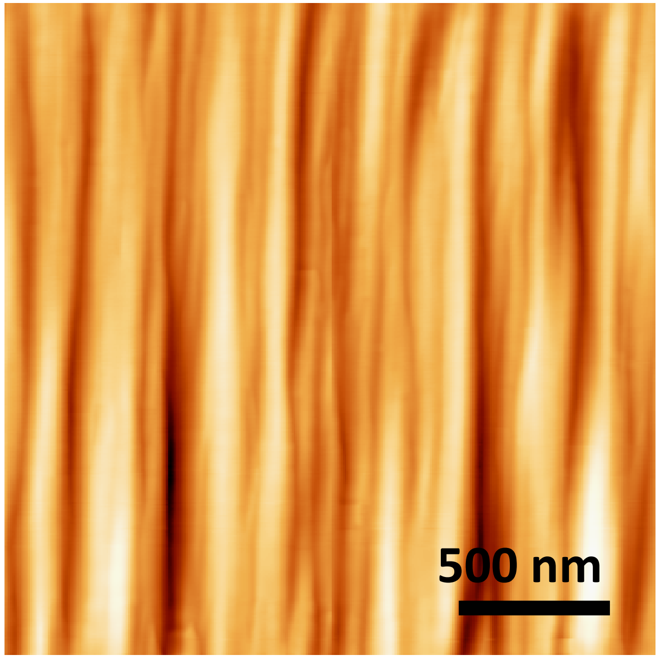
Step 2

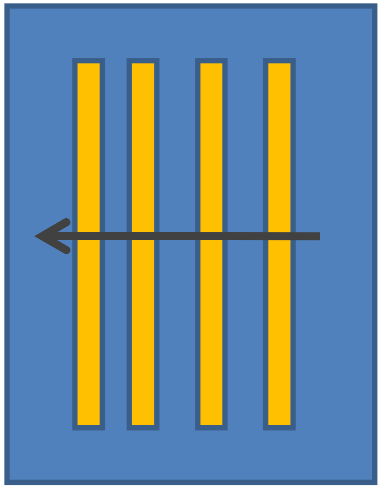
Ar+ ion flux

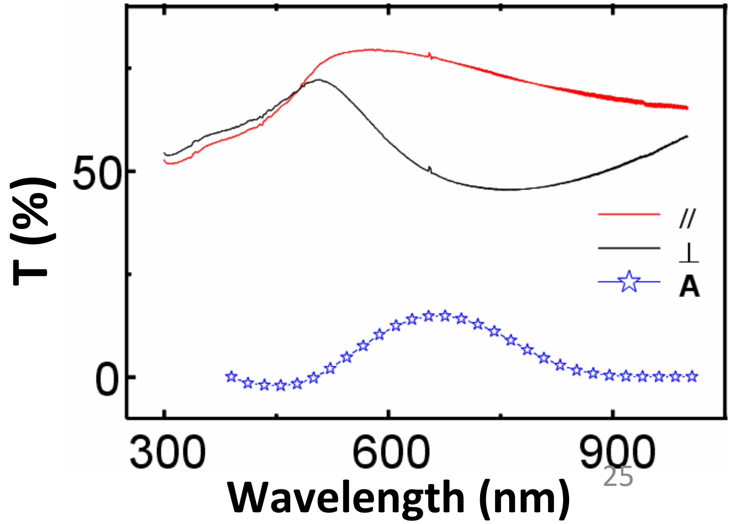
Step 3

Sample B
Gold 20 nm

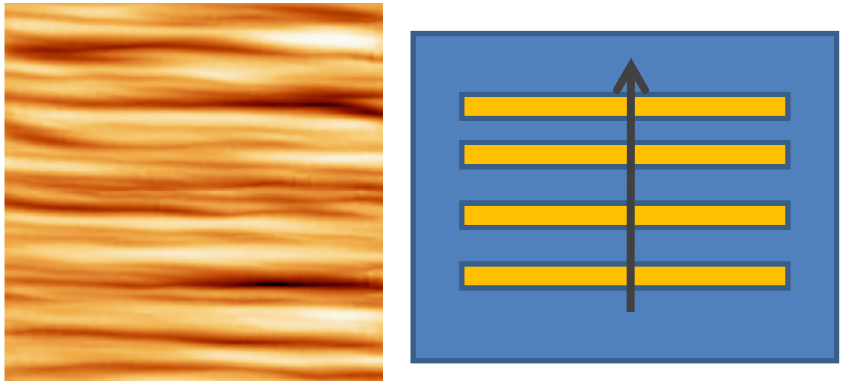
160 nm

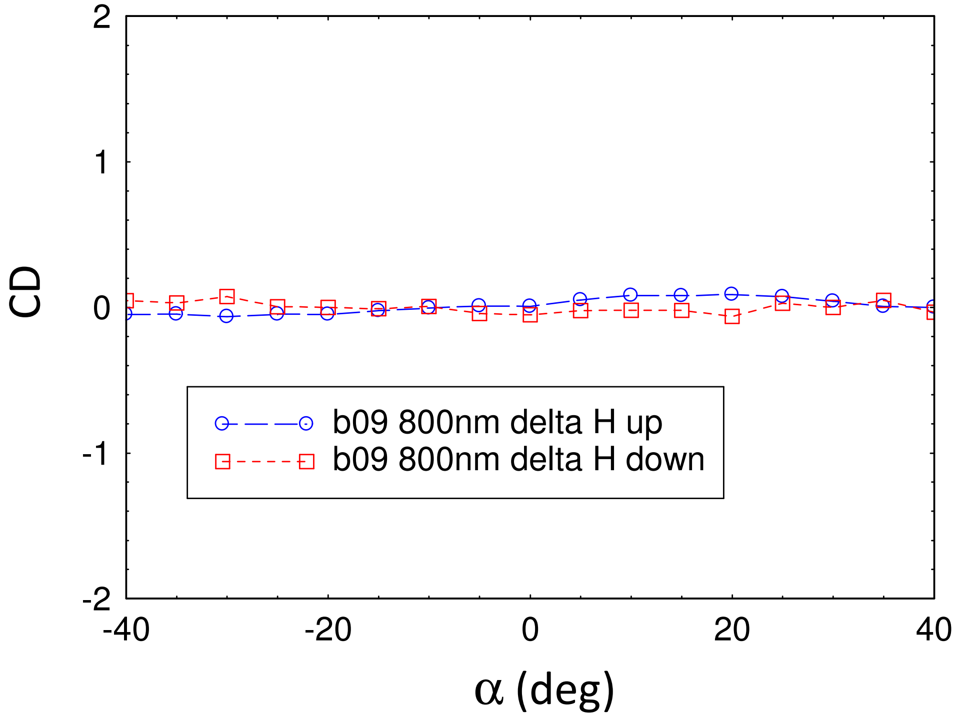


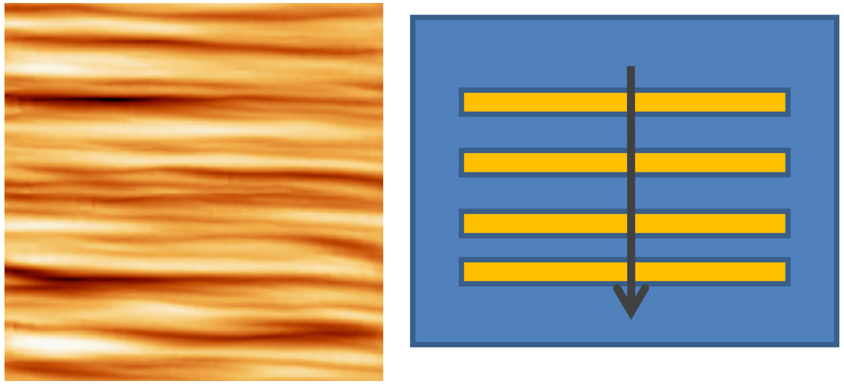




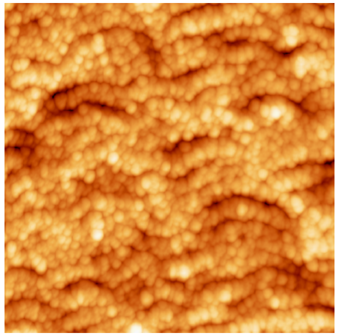
Linear measurements on sample B - P pol

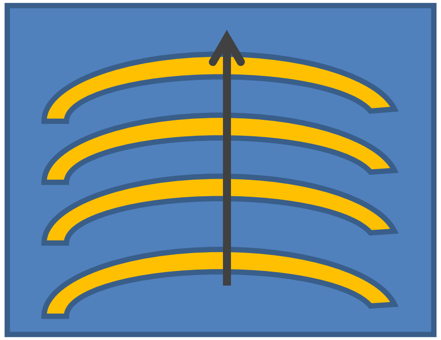


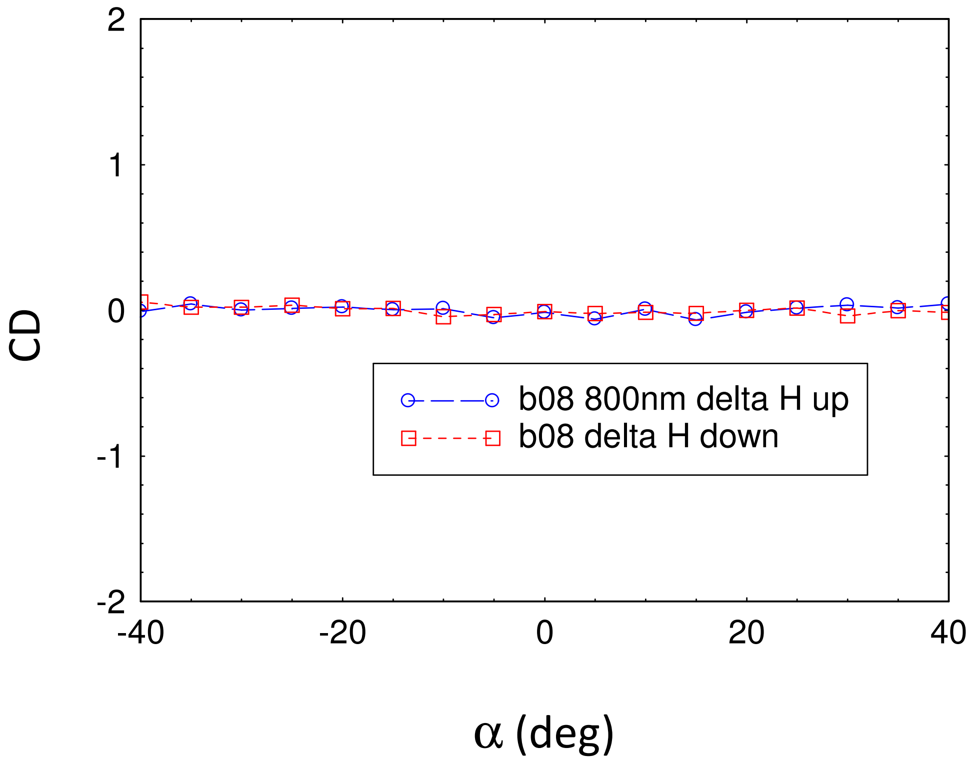


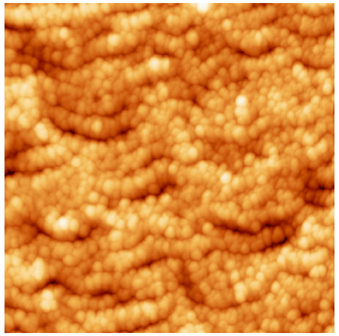


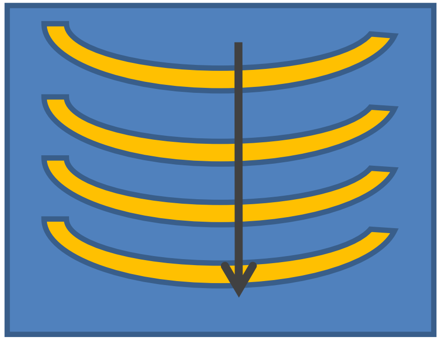
Linear measurements on sample A - P pol





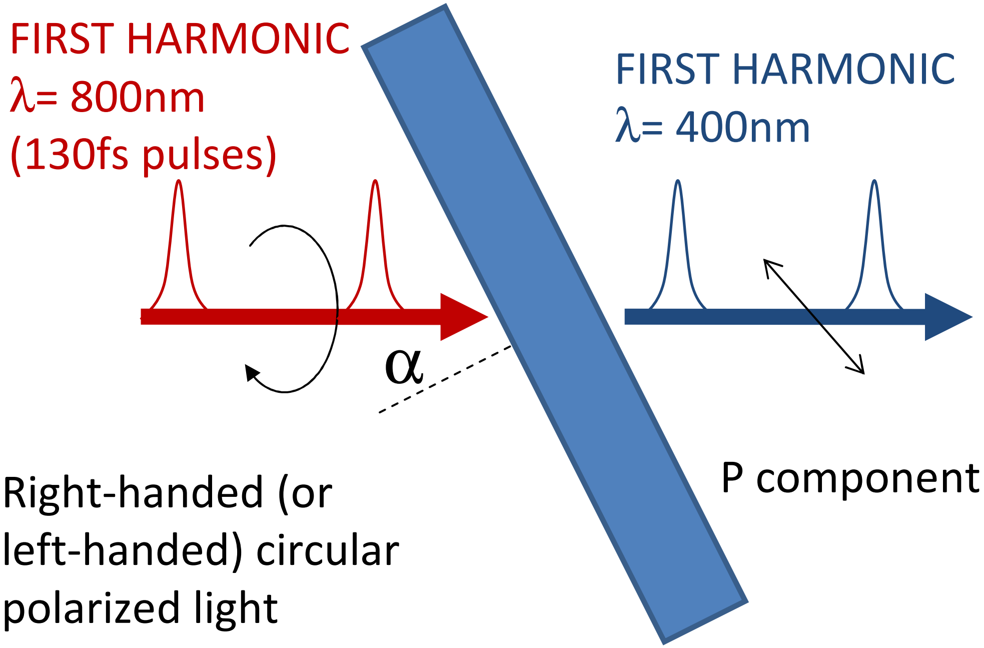






SHG measurements – P pol

The measurements were performed as a function of the incidence angle α


FIRST HARMONIC
λ= 800nm
(130fs pulses)

FIRST HARMONIC
λ= 400nm

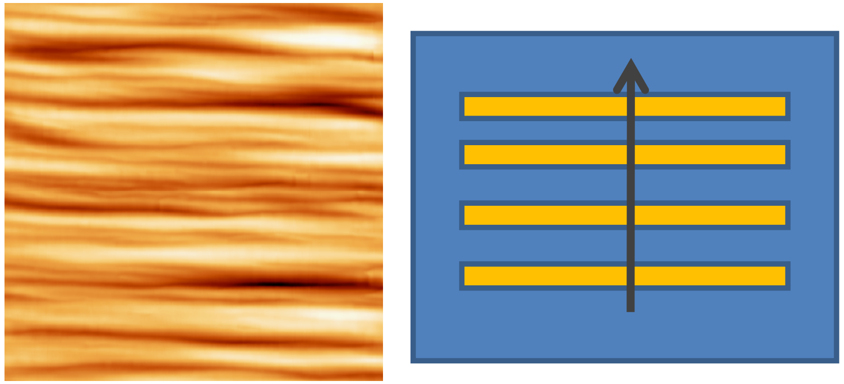
Right-handed (or
left-handed) circular
polarized light

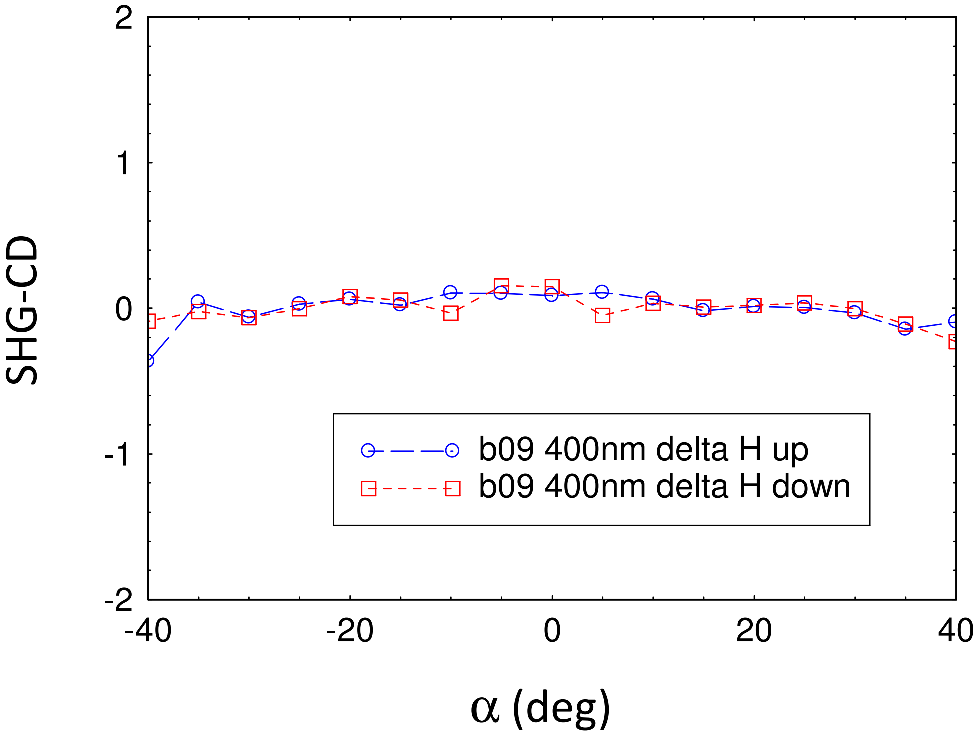
P component

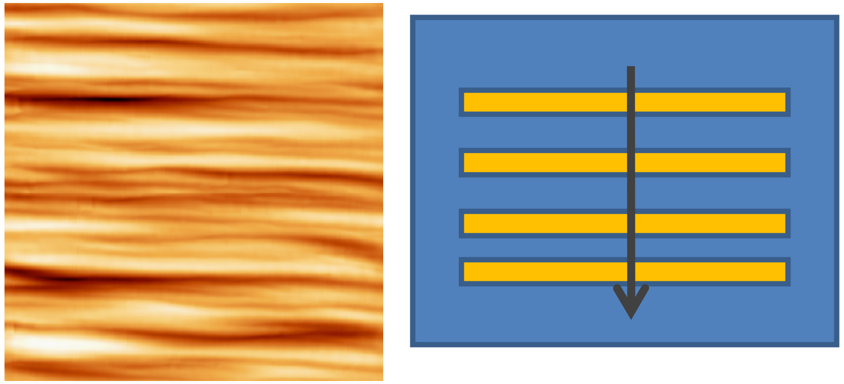
Second harmonic
generation - circular
dichroism (SHG-CD)

$$SHG-CD=\frac{I_L^{2\omega}-I_R^{2\omega}}{(I_L^{2\omega}+I_R^{2\omega})/2}$$

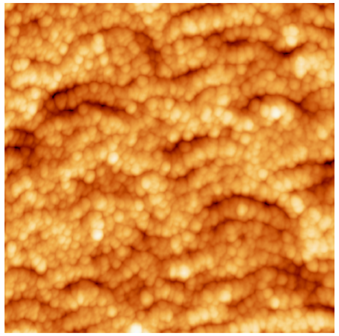
SHG measurements on sample B – P pol

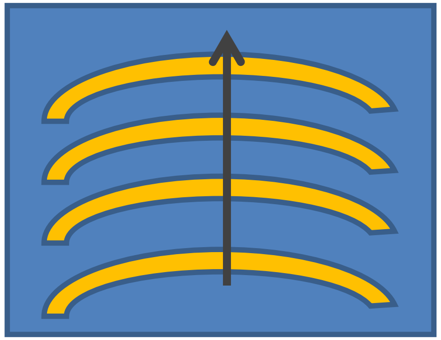


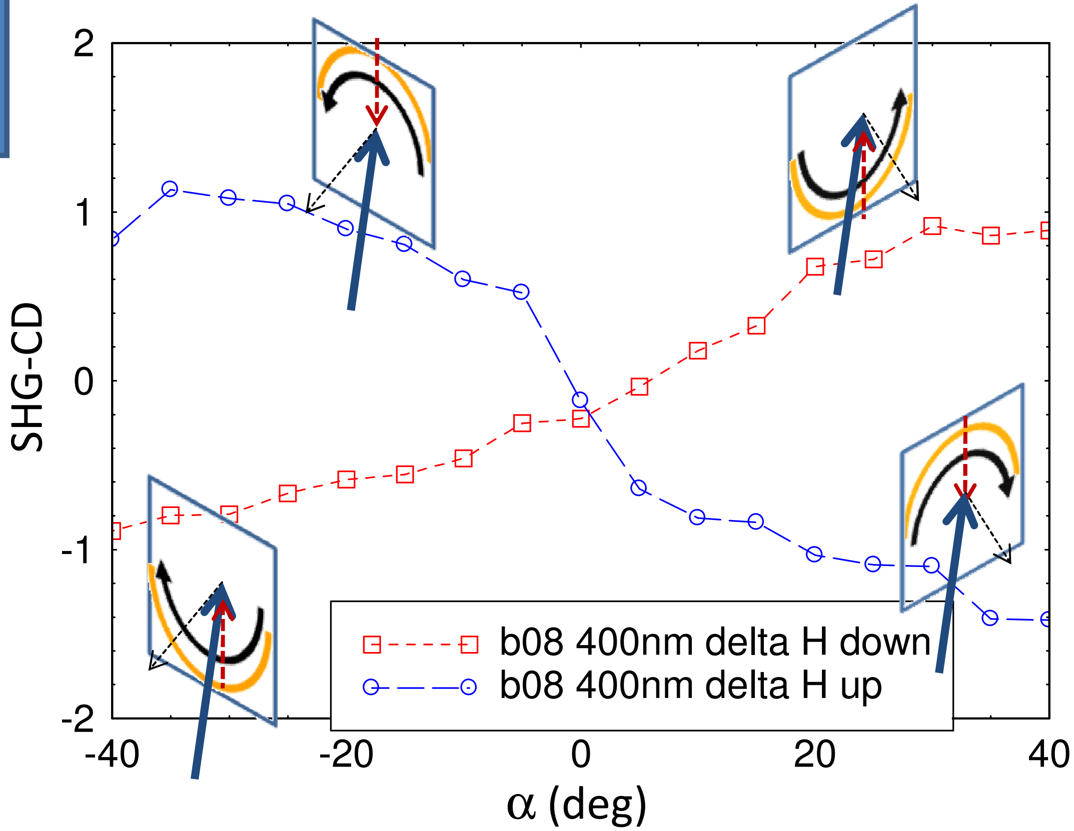


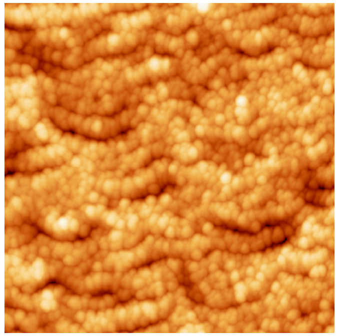


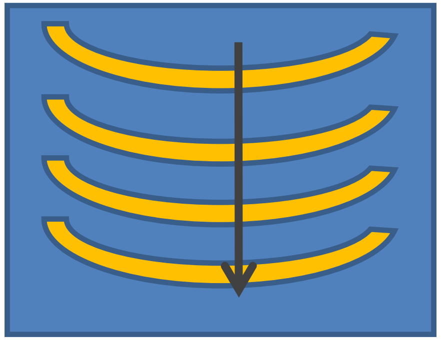
SHG measurements on sample A – P pol











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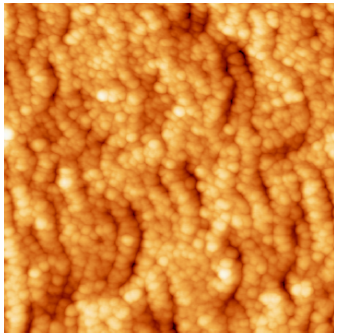
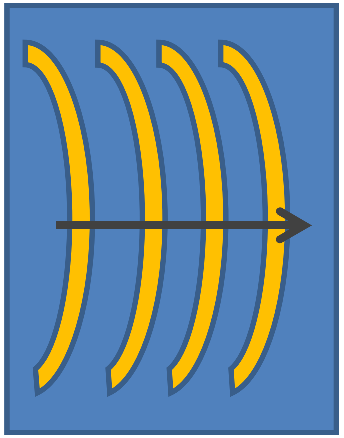
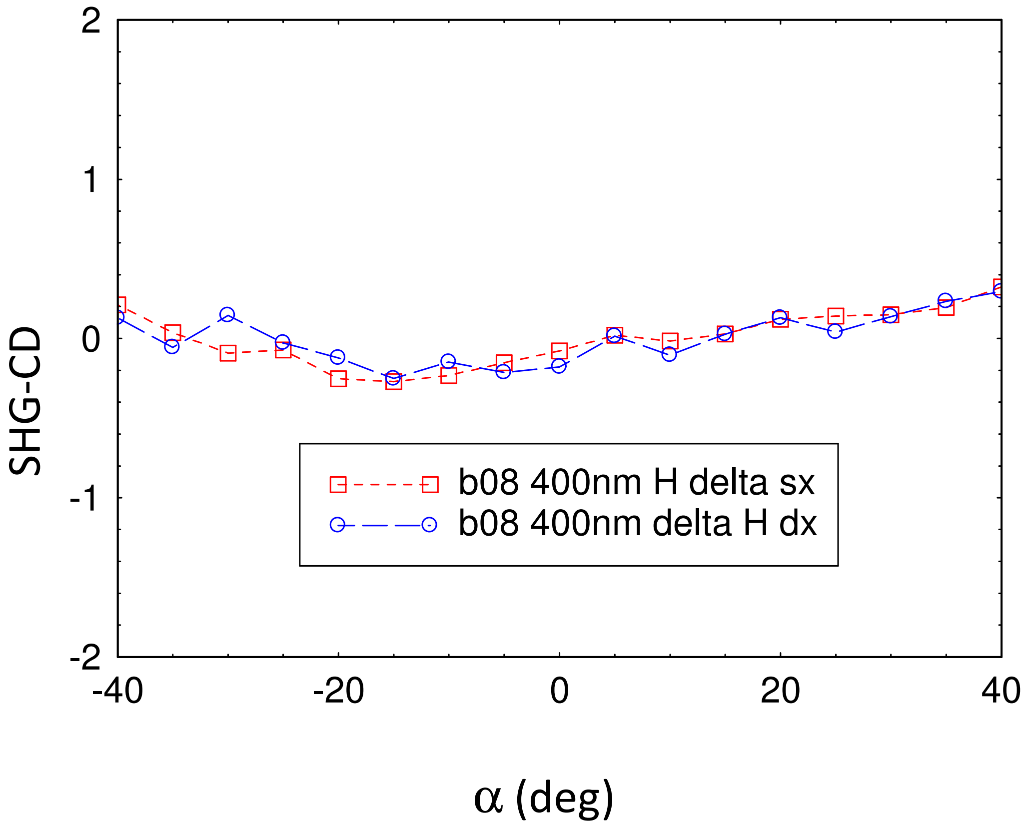
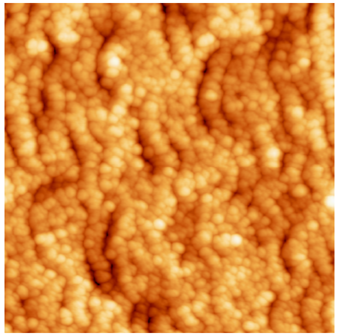
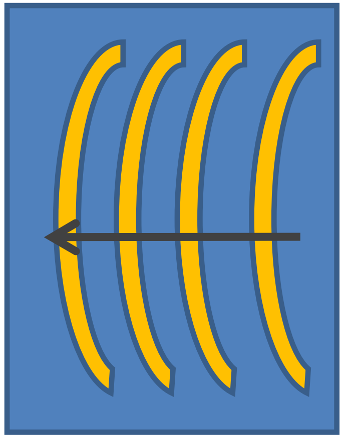
SHG measurements on sample A – P pol



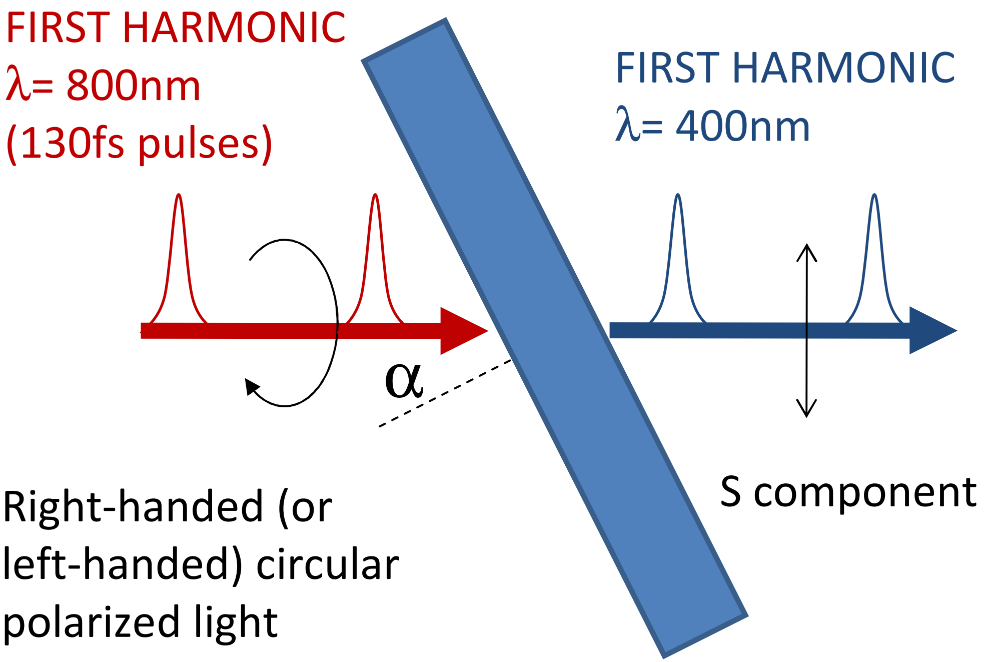








SHG measurements – S pol



FIRST HARMONIC
λ= 800nm
(130fs pulses)

FIRST HARMONIC
λ= 400nm

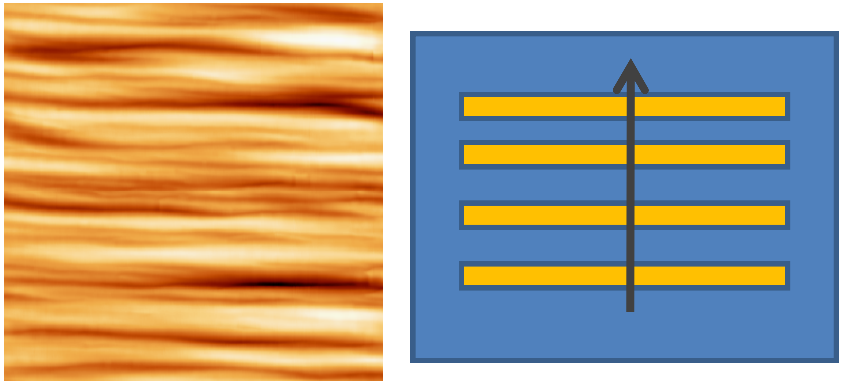
Right-handed (or left-handed) circular polarized light

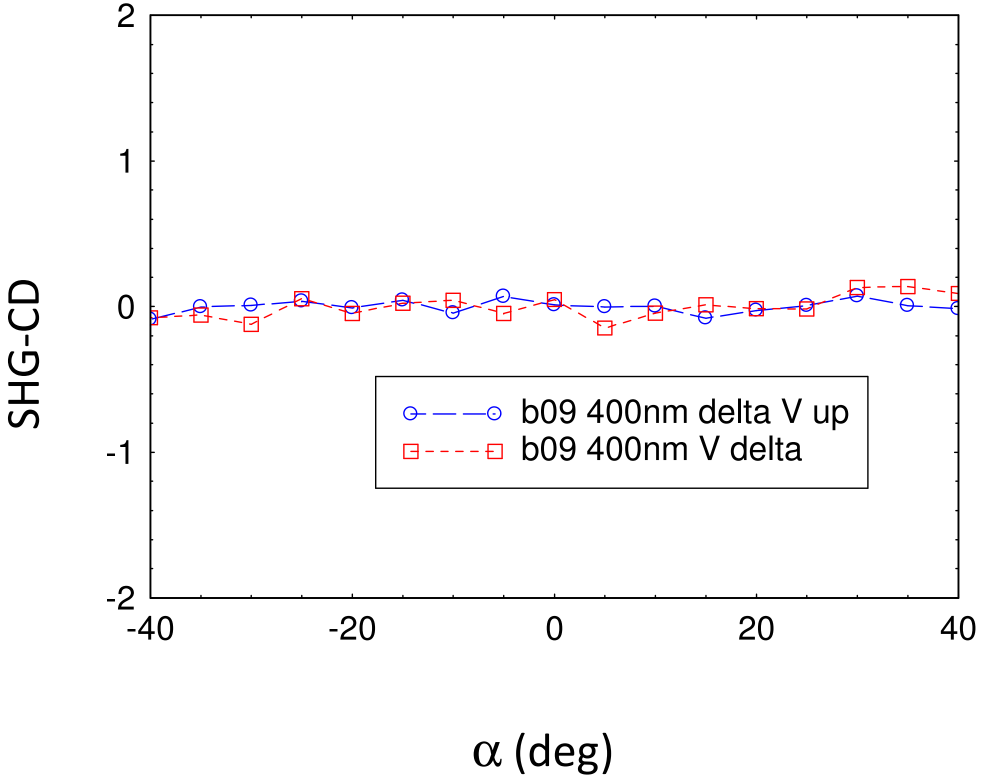
S component

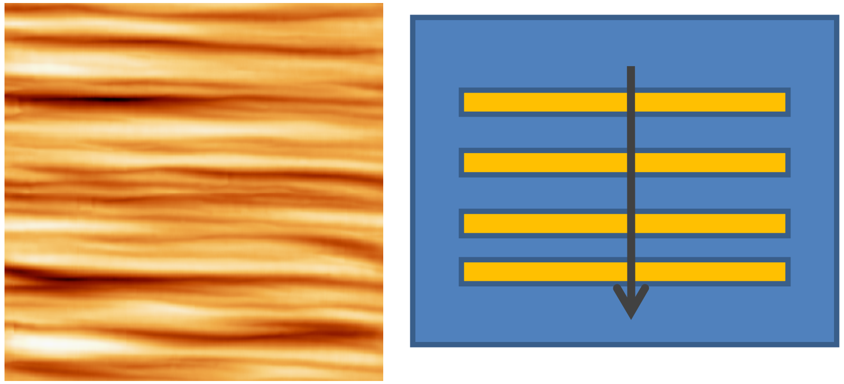
Second harmonic generation - circular dichroism (SHG-CD)

$$SHG-CD=\frac{I_L^{2\omega}-I_R^{2\omega}}{(I_L^{2\omega}+I_R^{2\omega})/2}$$

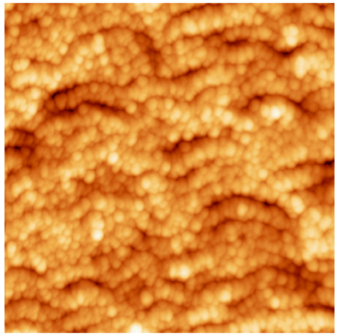
SHG measurements on sample B – S pol

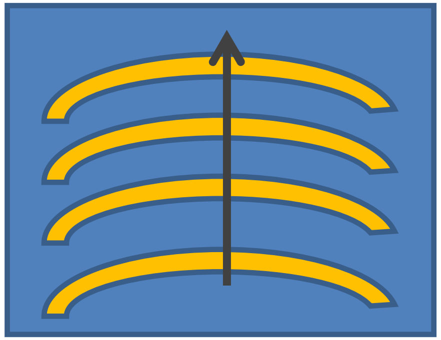


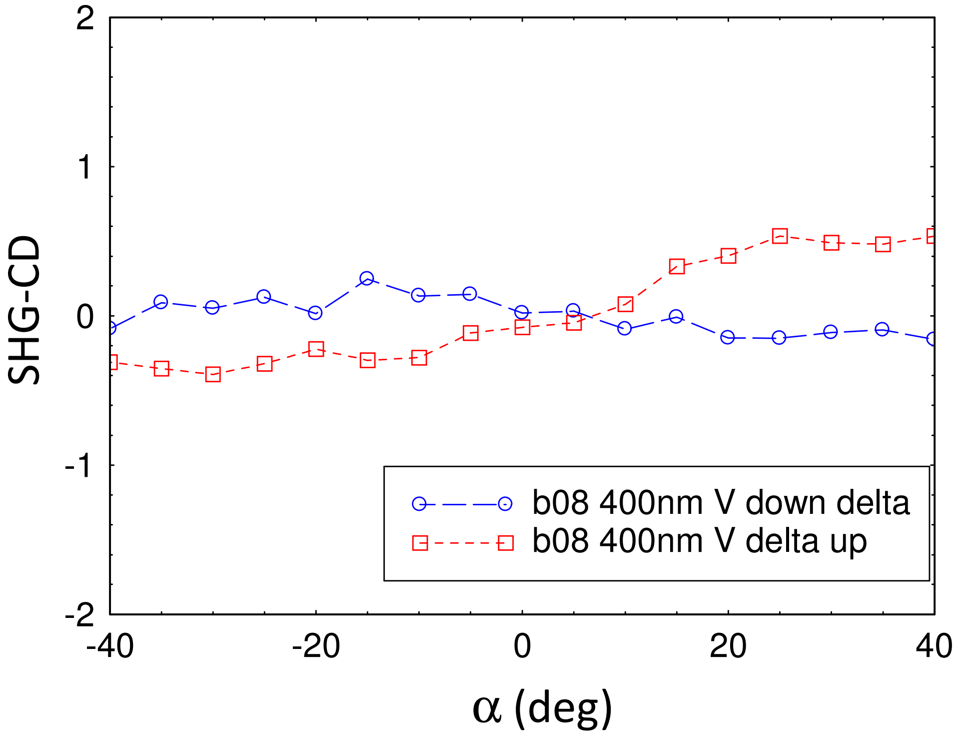


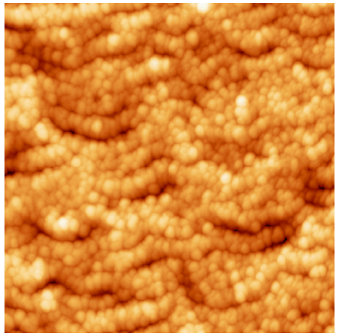


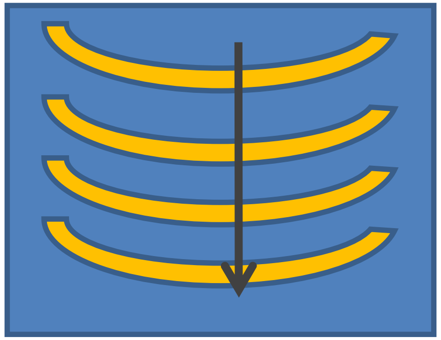
SHG measurements on sample A – S pol







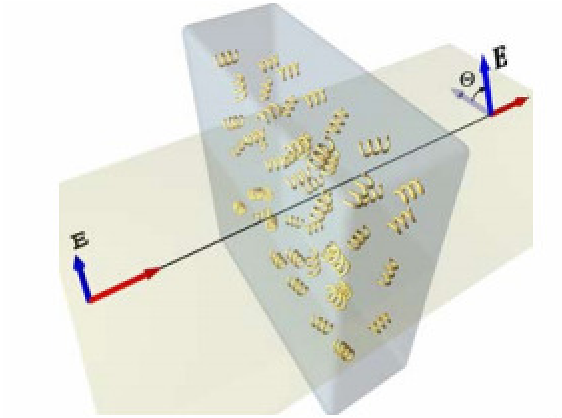


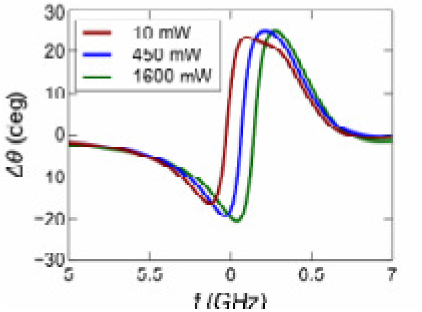


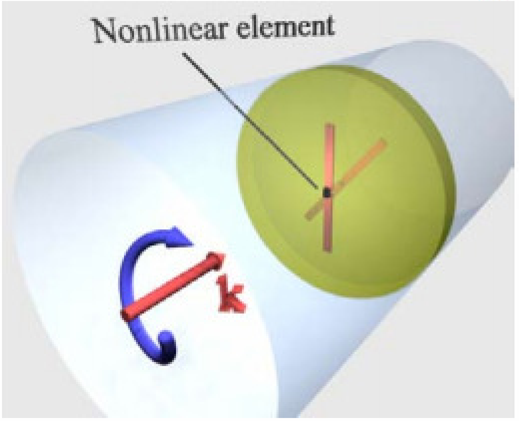
Chiral Metamaterials
Unlocking Nonlinear Optical Activity
Intensity dependent effects

AOS News Volume 25 Number 1 2011

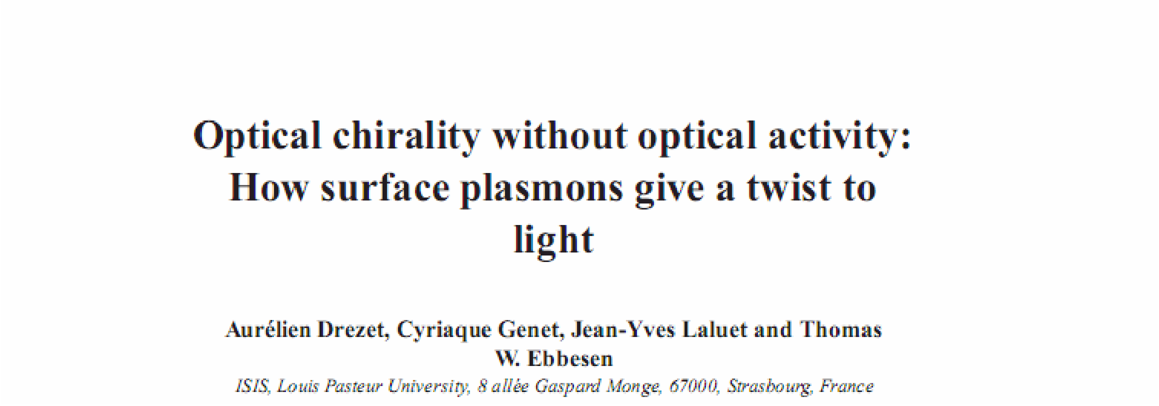
by David A. Powell, Ilya V. Shadrivov, Vassili A. Fedotov, Nikolay I. Zheludev and Yuri S. Kivshar





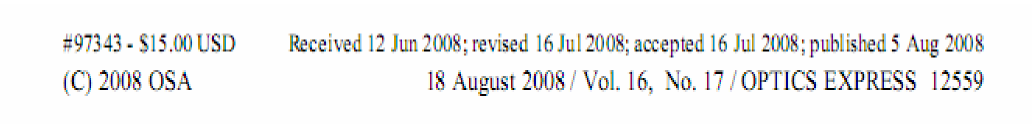


Optical diode for
cicular polarized
ligth



Optical chirality without optical activity: How surface plasmons give a twist to light

Aurélien Drezet, Cyriaque Genet, Jean-Yves Laluet and Thomas W. Ebbesen
ISIS, Louis Pasteur University, 8 allée Gaspard Monge, 67000, Strasbourg, France



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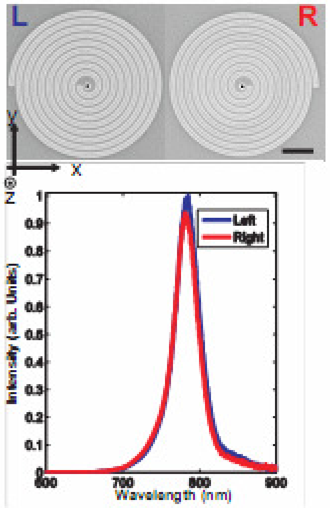

Fig. 1. Chiral plasmonic metamolecules. On the top panel: scanning electron micrographs of the left (L) and right (R) handed enantiomer (mirror image) planar chiral structures investigated. The scale bar is 3 μm long. The parameters characterizing the structure are the

- 3D, 2D-chirality, Extrinsic chirality
- SHG as chirality detection method
- Nonlinear measurements
- Intensity dependence

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Thank you !!!