SECOND ORDER NONLINEAR PROCESSES AT SURFACES AND INTERFACES

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- Boundary conditions of a polarized sheet
- Radiation from a polarized sheet
- Surface nonlinear response
- Bulk nonlinear response
- The equivalence of surface and bulk contributions
- The thin film geometry - example of an isotropic film
- Rotational anisotropy; examples

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Applications of nonlinear optical phenomena:

- development of optical-device technology and laser systems
- the use of these phenomena as a tool for material characterization
- particular case: **surface specificity of the second order nonlinear processes for centrosymmetric materials**

Within the electric dipole approximation the polarization can be written as an expansion of the electric field:

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

The inversion symmetry is reflected in the susceptibility tensor $\overset{\tau}{\chi}^{(n)}$ which is invariant under the transformation **r** $\rightarrow$ **-r**; this gives

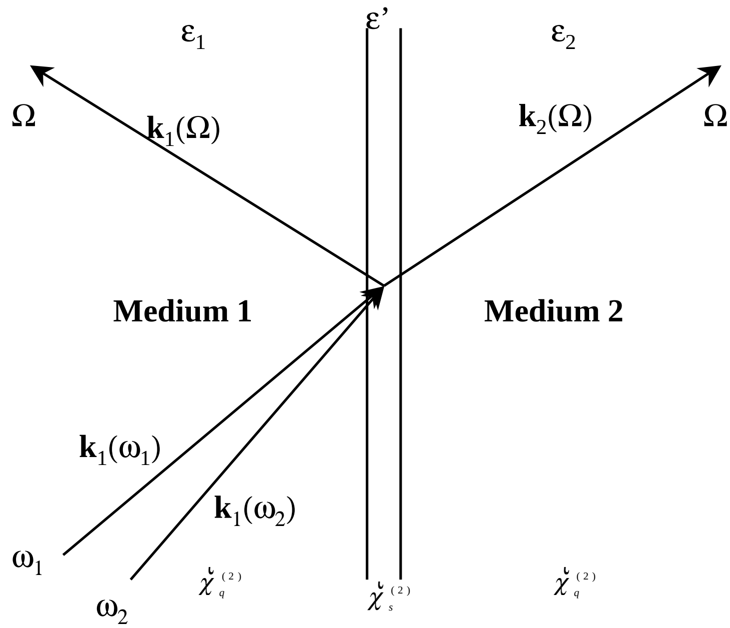
$$\overset{\tau}{\chi}^{(n)} = (-1)^{n+1} \overset{\tau}{\chi}^{(n)}$$

$\Rightarrow$ *any even-order response is forbidden within the electric dipole approximation for a centro-symmetrical material*

At the interface between two centro-symmetric media, the inversion symmetry is broken by definition, giving rise to an ED allowed second order susceptibility

$\Rightarrow$ second order processes are useful nondestructive techniques for the study of surfaces and buried interfaces, with a resolution better than the inherent penetration depth of the probe

Boundary conditions of a polarized sheet



The nonlinearity of the interface is treated as a sheet of generalized nonlinear source polarization. From Maxwell’s equations with a nonlinear source polarization $\boldsymbol{P}^{nls}$ occupying a finite volume:

$$\nabla \cdot \boldsymbol{D} = -4\pi \nabla \cdot \boldsymbol{P}^{nls}$$

$$c \nabla \times \boldsymbol{E} + \frac{\partial B}{\partial t} = 0$$

$$\nabla \cdot \boldsymbol{B} = 0$$

$$c \nabla \times \boldsymbol{H} - \frac{\partial D}{\partial t} = 4\pi \frac{\partial P^{nls}}{\partial t}$$

the boundary conditions for the electric and magnetic fields on either side of this polarized sheet $\boldsymbol{P}_s^{nls}(x,y)$ (with a volume polarization $\boldsymbol{P}_s^{nls}(x,y)\delta(z)$) are:

$$\Delta D_z = -4\pi \nabla \cdot \boldsymbol{P}_s^{nls}$$

$$\Delta E_t = -\frac{4\pi}{\varepsilon'} \nabla_t P_{s,z}^{nls}$$

$$\Delta B_z = 0$$

$$\Delta H_t = \frac{4\pi}{c} \frac{\partial P_s^{nls}}{\partial t} \times \hat{z}$$

Radiation from a polarized sheet

$$\boldsymbol{P}_s^{nls}(x,y,t) = \boldsymbol{P}_s e^{ipx-i\Omega t} + c.c.$$

The reflected beam is given by the wave vector $\mathbf{k}_1 = p\hat{x} - q_1\hat{z}$, with $q_1 = [\varepsilon_1 K^2 - p^2]^{1/2}$; similarly, the transmitted beam is given by $\mathbf{k}_2 = p\hat{x} + q_1\hat{z}$. From the boundary conditions, the radiated fields are (with $\varepsilon_1 = \varepsilon_2 = \varepsilon' = 1$):

$$\boldsymbol{E}_i(x,y,z,t) = \boldsymbol{E}_i(\Omega)e^{i\boldsymbol{k}_i\cdot\boldsymbol{r}-i\Omega t} + c.c.$$

where: $$\boldsymbol{E}_i = \frac{2\pi i K^2}{q_i}\,[\boldsymbol{P}_s - \hat{k}_i(\hat{k}_i\cdot\boldsymbol{P}_s)]$$

The Fresnel corrections are made for the waves propagating towards the interface by replacing $\hat{e}_i$ with $e = \boldsymbol{F}_{i\to j}\hat{e}_i$, where the Fresnel transformation has the diagonal elements (for isotropic media):

$$F_{i\to j}^{xx} = \frac{2\varepsilon_i q_j}{\varepsilon_j q_i + \varepsilon_i q_j}\ ;\ F_{i\to j}^{yy} = \frac{2q_i}{q_i + q_j}\ ;\ F_{i\to j}^{zz} = 2\frac{\varepsilon_1\varepsilon_2}{\varepsilon'}\frac{q_i}{\varepsilon_j q_i + \varepsilon_i q_j}$$

The radiated field can be written like

$$\hat{e}_i\cdot E_i = \frac{2\pi i K}{\varepsilon_i^{1/2}}\sec\theta_i\,(e\cdot P_s)$$

where $\sec\theta_i(\Omega) = \dfrac{\Omega\varepsilon_i^{1/2}(\Omega)}{cq_i(\Omega)}$ defines, for a lossless medium, the angle between the wave at Ω and the surface normal.

Surface nonlinear response

When considering the nonlinear polarized sheet as arising from the surface nonlinear susceptibility tensor $\overleftrightarrow{\chi}_s^{(2)}$:

$$\boldsymbol{P}_s(\Omega) = \overleftrightarrow{\chi}_s^{(2)}(\Omega = \omega_1 + \omega_2) : \boldsymbol{E}(\omega_1)\boldsymbol{E}(\omega_2)$$

or

$$\boldsymbol{P}_s(\Omega) = \overleftrightarrow{\chi}_s^{(2)}(\Omega = \omega_1 + \omega_2) : e_{i1}(\omega_1) e_{i2}(\omega_2) E_{i1}(\omega_1) E_{i2}(\omega_2)$$

The radiated fields can be now written as

$$\hat{e}_i(\Omega) \cdot E_i(\Omega) = \frac{2\pi i \Omega \sec\theta_i(\Omega)}{c\varepsilon_i^{1/2}(\Omega)} [e(\Omega) \cdot \chi_s^{(2)} : e(\omega_1) e(\omega_2)] E_{i_1}(\omega_1) E_{i_2}(\omega_2)$$

When absorption is present in the bulk media, the electric field amplitudes correspond to the incoming or outgoing fields near the interface.

For an arbitrary geometry of the pump beams, the direction of the radiated beam is given by the in-plane wave vector components

$\mathbf{p}(\Omega) = \mathbf{p}(\omega_1) + \mathbf{p}(\omega_2)$ - the nonlinear Snell's law

In terms of irradiances ($I = c\varepsilon^{1/2}|E|^2/2\pi$ for a plane wave in a medium ε), the fields are given by

$$I_i(\Omega) = \frac{8\pi^3 \Omega^2 \sec^2\theta_i(\Omega)}{c^3[\varepsilon_i(\Omega)\varepsilon_{i_1}(\omega_1)\varepsilon_{i2}(\omega_2)} |e(\Omega) \cdot \chi_s^{(2)} : e(\omega_1) e(\omega_2)|^2 \, I_{i_1}(\omega_1) I_{i_2}(\omega_2)$$

Bulk nonlinear response

The nonlinear source polarization in the bulk of a material, as a multipole expression in succesive degrees of nonlocality, is:

$$
\begin{aligned}
\boldsymbol{P}^{nls}(\Omega) = {} & \chi^{(2)}(\Omega=\omega_1+\omega_2):\boldsymbol{E}(\omega_1)\boldsymbol{E}(\omega_2) + \\
& \frac{1}{2}\overleftrightarrow{\chi}_q^{(2)}(\Omega=\omega_1+\omega_2):\boldsymbol{E}(\omega_1)\nabla\boldsymbol{E}(\omega_2) + \\
& \frac{1}{2}\overleftrightarrow{\chi}_q^{(2)}(\Omega=\omega_1+\omega_2):\boldsymbol{E}(\omega_2)\nabla\boldsymbol{E}(\omega_1) + \ldots
\end{aligned}
$$

The relative contributions of the succesive terms vary like (ka), with <u>a</u> the typical atomic dimension. For centrosymmetric media, the leading-order response consists of the electric-quadrupole and magnetic-dipole terms comprised of products of $\boldsymbol{E}$ and the spatial derivatives of $\boldsymbol{E}$. Up to the first order spatial derivatives of the electric field, we can express the generalized polarization like:

$$
\boldsymbol{P}^{(2)}(\Omega) = \boldsymbol{P}_d^{(2)}(\Omega) - \nabla\cdot\overleftrightarrow{Q}^{(2)}(\Omega) + \frac{c}{i\Omega}\nabla\times\boldsymbol{M}^{(2)}(\Omega)
$$

where, in the case of SHG, we can write:

$$
\begin{aligned}
\boldsymbol{P}_d^{(2)} &= \overleftrightarrow{\chi}^{D}:\boldsymbol{E}(\omega)\boldsymbol{E}(\omega) + \overleftrightarrow{\chi}^{P}:\boldsymbol{E}(\omega)\nabla\boldsymbol{E}(\omega) \\
\overleftrightarrow{Q}^{(2)} &= \overleftrightarrow{\chi}^{Q}:\boldsymbol{E}(\omega)\boldsymbol{E}(\omega) \\
\boldsymbol{M}^{(2)} &= \overleftrightarrow{\chi}^{M}:\boldsymbol{E}(\omega)\boldsymbol{E}(\omega)
\end{aligned}
$$

with $\overleftrightarrow{\chi}^{D}$ describing a local response, while $\overleftrightarrow{\chi}^{P}$, $\overleftrightarrow{\chi}^{Q}$ and $\overleftrightarrow{\chi}^{M}$ are nonlocal.

For nonmagnetic materials (inversion symmetry in both space and time), $\boldsymbol{M}^{(2)}(\Omega) = 0$.

The effective SH polarization can be written as:

$$P_i(\Omega) = \gamma\nabla_i(\boldsymbol{E}\cdot\boldsymbol{E}) + (\delta\text{-}\beta\text{-}2\gamma)(\boldsymbol{E}\cdot\nabla)E_i + \beta(\nabla\cdot\boldsymbol{E})E_i + \zeta E_i\nabla_i E_i$$

* β, γ and δ describe the isotropic response of the medium.
* for a homogeneous medium, $\nabla\cdot\boldsymbol{E} = 0$
* $(\delta\text{-}\beta\text{-}2\gamma)(\boldsymbol{E}\cdot\nabla)E_i = 0$ when only a single plane wave is present in the medium (reflections from deeper lying interfaces are ignored)
* in an isotropic material, $\zeta = 0$
* the only bulk term contributing to the signal in a simple measurement of an isotropic medium remains $\gamma\nabla_i(\boldsymbol{E}\cdot\boldsymbol{E})$ which is a longitudinal field for any pump field $\boldsymbol{E}$, giving rise to radiation fields indistinguishable from those of an equivalent surface nonlinear response

The equivalence of surface and bulk contributions

For a bulk nonlinear source polarization given by a single wave vector $\boldsymbol{k}_b$:

$$\boldsymbol{P}(x,y,z,t) = \boldsymbol{P}_b(\Omega,\boldsymbol{k}_b)e^{i\boldsymbol{k}_b\cdot\boldsymbol{x}-i\Omega t}\vartheta(z) + c.c.$$

one can define an equivalent nonlinear polarization sheet at the interface between media 1 and 2:

$$\boldsymbol{P}_s^{eq}(x,y,z,t) = \boldsymbol{P}_s^{eq}(\Omega,\boldsymbol{k}_b)e^{i\boldsymbol{k}_b\cdot\boldsymbol{x}-i\Omega t}\delta(z) + c.c.$$

Taking the bulk polarization as a succession of polarized sheets and considering the propagation of the nonlinear wave in medium 2, the equivalent polarization sheet is given by

$$\boldsymbol{P}_s^{eq}(\Omega,\boldsymbol{k}_b) = \frac{i}{q_b+q_2}\left[P_{b,x}(\Omega,k_b)\hat{x} + P_{b,y}(\Omega,k_b)\hat{y} + \frac{\varepsilon'(\Omega)}{\varepsilon_2(\Omega)}P_{b,z}(\Omega,k_b)\hat{z}\right]$$

where q_b is the z-component of $\boldsymbol{k}_b$ and q_2 is the z-component of the Ω-wave in medium 2.

The bulk nonlinear polarization $\boldsymbol{P}_b(\Omega) = \gamma\nabla_i(\boldsymbol{E}\cdot\boldsymbol{E})$ excited by a single plane wave can be written as $\boldsymbol{P}_b(\Omega) = i\gamma\boldsymbol{k}_s[\boldsymbol{E}(\omega)\cdot\boldsymbol{E}(\omega)]$. Defining an effective surface polarization $\boldsymbol{P}_s^{eq}(\Omega)$ corresponding to this term and looking at the p-polarized radiation which it produces, one finds:

$$\boldsymbol{e}_p\cdot\boldsymbol{P}_s^{eq}(\Omega) = C\left[q_2\hat{x} + \frac{\varepsilon_2}{\varepsilon'}p\hat{z}\right]\cdot\left\{[-\gamma(\boldsymbol{E}\,\boldsymbol{E})(q_s+q_2)^{-1}]\left[p\hat{x} + \frac{\varepsilon'}{\varepsilon_2}q_2\hat{z}\right]\right\}$$

$$= -C\gamma p(\boldsymbol{E}\,\boldsymbol{E})$$

$$= \boldsymbol{e}_p\cdot\left[-\gamma\frac{\varepsilon'}{\varepsilon_2}(\boldsymbol{E}\,\boldsymbol{E})\hat{z}\right]$$

$$= \boldsymbol{e}_p\cdot\boldsymbol{P}_s^{\gamma}(\Omega)$$

where we have defined a surface polarization

$$\boldsymbol{P}_s^{\gamma}(\Omega) = -\gamma\frac{\varepsilon'}{\varepsilon_2}(\boldsymbol{E}(\omega)\,\boldsymbol{E}(\omega))\hat{z}$$

By specifying the radiated field in terms of a surface polarization $\boldsymbol{P}_s^{\gamma} \parallel \hat{z}$ one can reproduce the angular and polarization dependence of the bulk longitudinal polarization, without introducing the vector $\boldsymbol{k}_s$. It is therefore impossible to separate the bulk longitudinal polarization from the z-component of the surface polarization.

This equivalence has also been demonstrated for an arbitrary pump field, in isotropic as well as in cubic materials.

The SH response from an interface between two bulk centrosymmetric media can be described by an effective surface nonlinear tensor

$$\chi^{(2)}_{s,eff} = \chi^{(2)}_{s} + \chi^{(2)}_{s,\gamma}$$

with the radiated field expressed like

$$\hat{e}_i(\Omega)\cdot E_i(\Omega) = \frac{2\pi i\Omega \sec\theta_i(\Omega)}{c\varepsilon_i^{1/2}(\Omega)}[e(\Omega)\cdot\chi^{(2)}_{s,eff} : e(\omega_1)e(\omega_2)]E_{i_1}(\omega_1)E_{i_2}(\omega_2)$$

Table 1

Independent nonvanishing elements of $\chi_s^{(2)}$ for crystallographic and continuous point groups for a surface in the xy-plane (Giordmaine 1965). When mirror planes are present, one of them is always perpendicular to $\hat{y}$. For SHG, $\chi^{(2)}_{s,ijk} = \chi^{(2)}_{s,ikj}$ and elements related by permutation of the last two indices have been omitted. For SFG, these elements are generally distinct; any symmetry constraints are indicated in parentheses. The terms enclosed entirely in parentheses are antisymmetric elements only present for SFG.

Symmetry class	Independent non-vanishing elements of $\chi_s^{(2)}$
1	$xxx, xxy, xyy, yxx, yxy, yyy$
	$xxz, xyz, yxz, yyz, zxx, zxy, zyy, xzz, yzz, zxz, zyz, zzz$
m	$xxx, xyy, xzz, xzx, yzy, yxy, zxx, zyy, zxz, zzz$
2	$xzx, xyz, yxz, yzy, zxx, zyy, zxy, zzz$
mm2	xzx, yzy, zxx, zyy, zzz
3	$xxx = -xyy = -yyx\ (= -yxy)$
	$yyy = -yxx = -xyx\ (= -xxy), yzy = xzx, zxx = zyy, xyz = -yxz$
	$zzz, (zxy = -zyx)$
3m	$xxx = -xyy = -yxy\ (= -yyx)$
	$xzx = yzy$
	$zxx = zyy, zzz$
4, 6, ∞	$xxz = yyz, zxx = zyy, xyz = -yxz, zzz, (zxy = -zyx)$
4mm, 6mm, ∞m	$xxz = yyz, zxx = zyy, zzz$

Thin film geometry

* offers additional possibilities for the problem of the SHG vs. bulk separation.
* important for the study of buried interfaces in case of overlayers having thicknesses of the order of the wavelength of light

The total SH field generated by a nonlinear film is given by:

$$\boldsymbol{E}(\Omega) = \boldsymbol{E}^B(\Omega) + \boldsymbol{E}^S(\Omega) + \boldsymbol{E}^I(\Omega)$$

with a total SH output:

$$S(\Omega) = \frac{32\pi^3\omega}{\eta c^3\varepsilon_q^{1/2}(\Omega)\varepsilon_q(\omega)}\sec^2\theta_\Omega\left|\chi_{eff}^{(2)}\right|^2 I^2(\omega)AT$$

where

$$\chi_{eff}^{(2)} = \vec{e}(\Omega)\cdot\overset{\tau}{L}(\Omega,z=0):\overset{\tau}{\chi}{}_S^{(2)}:\overset{\tau}{L}(\omega,z=0)\vec{e}(\omega)\overset{\tau}{L}(\omega,z=0)\vec{e}(\omega)$$
$$+\vec{e}(\Omega)\overset{\tau}{L}(\Omega,z=d):\overset{\tau}{\chi}{}_I^{(2)}:\overset{\tau}{L}(\omega,z=d)\vec{e}(\omega)\overset{\tau}{L}(\omega,z=d)\vec{e}(\omega)$$
$$+\int_0^d \vec{e}(\Omega)\overset{\tau}{L}(\Omega,z'):\overset{\tau}{\chi}{}_B^{(2)}:\overset{\tau}{L}(\omega,z')\vec{e}(\omega)\overset{\tau}{L}(\omega,z')\vec{e}(\omega)dz'$$

θ_Ω is the exit angle, *A* the beam cross section, *T* the pulse width, $\vec{e}(\Omega)$ the unit vector of the field at Ω and $\overset{\tau}{L}(\omega,z)$ is a diagonal tensor describing the field inside the film, with the elements:

$$L_{xx}(\omega,z) = t_1^p\left(e^{ik_{fz}z} - r_I^p e^{ik_{fz}(2d-z)}\right)\frac{\cos\theta_f}{\cos\theta_\omega}$$

$$L_{yy}(\omega,z) = t_1^s\left(e^{ik_{fz}z} + r_I^s e^{ik_{fz}(2d-z)}\right)$$

$$L_{zz}(\omega,z) = t_1^p\left(e^{ik_{fz}z} + r_I^p e^{ik_{fz}(2d-z)}\right)\frac{\varepsilon_1^{1/2}}{\varepsilon_f^{1/2}}$$

$$t_1^h = \frac{t_S^h}{1 - r_S^h r_I^h e^{i2k_{fz}d}}$$

Because of the phase factors in $\breve{L}$, the bulk term in $\chi^{(2)}_{eff}$ will exhibit a composite interference pattern as the thickness d varies; the interface, surface and bulk term can have relative phase differences and their interference also changes with *d*. By fitting $S(2\omega)$ versus *d* one can get to the different surface and bulk susceptibilities.

The effective bulk SH polarization is written as:

$$P_i(\Omega) = \gamma\nabla_i(\mathbf{E}\cdot\mathbf{E}) + (\delta\text{-}\beta\text{-}2\gamma)(\mathbf{E}\cdot\nabla)E_i + \beta(\nabla\cdot\mathbf{E})E_i + \zeta E_i\nabla_i E_i$$

For an isotropic medium, one can express the parameters β, γ, δ and ζ as a function of the non-vanishing bulk susceptibilities:

$$\beta = 2(\overset{\tau}{\chi}{}^{P}_{iijj} - \overset{\tau}{\chi}{}^{Q}_{ijij})$$
$$\gamma = \overset{\tau}{\chi}{}^{P}_{ijij} - \overset{\tau}{\chi}{}^{Q}_{iijj}$$
$$\delta = 2(\overset{\tau}{\chi}{}^{P}_{iiii} - \overset{\tau}{\chi}{}^{Q}_{iiii})$$
$$\zeta = 0$$
$$\delta - \beta - 2\gamma = 2(\overset{\tau}{\chi}{}^{P}_{ijji} - \overset{\tau}{\chi}{}^{Q}_{ijij})$$

where $\overset{\tau}{\chi}{}^{Q}_{ijij} = \overset{\tau}{\chi}{}^{Q}_{ijji}$ and $\overset{\tau}{\chi}{}^{P,Q}_{iiii} = \overset{\tau}{\chi}{}^{P,Q}_{iijj} + \overset{\tau}{\chi}{}^{P,Q}_{ijij} + \overset{\tau}{\chi}{}^{P,Q}_{ijji}$

Since γ is indistinguishable from surface contribution, it will be accounted for by taking effective surface susceptibilities for the z direction. There will be 7 independent susceptibility elements, probed for various polarizations combinations:

	s/p	m/s	p/p	m/p
$\chi_{S,zyy} - \gamma$	●		●	●
$\chi_{I,zyy} + \gamma$				
$\chi_{S,zzz} - \gamma$			●	●
$\chi_{I,zzz} + \gamma$				
$\chi_{S,yzy}$		●	●	●
$\chi_{S,yzy}$				
$\delta - \beta - 2\gamma$		●	●	●

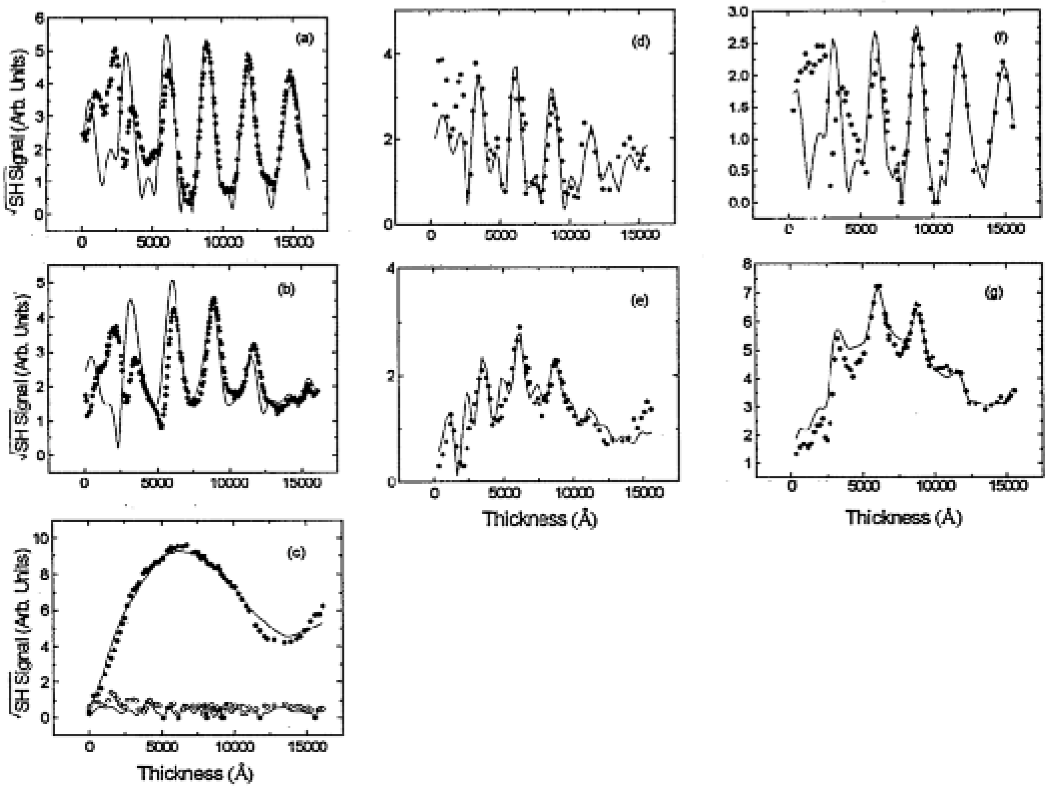


FIG. 3. SHG vs film thickness from a C_{60} film grown at room temperature. The lines are the theoretical fit to the experimental data (circles). (a) Fundamental input s polarized and reflected SH output p polarized. (b) Fundamental input s polarized and transmitted SH output p polarized. (c) Fundamental input p polarized and reflected SH output p polarized (open circles) fundamental input p polarized and transmitted SH output p polarized (solid circles). (d) Fundamental input mixed polarized and reflected SH output s polarized. (e) Fundamental input mixed polarized and transmitted SH output s polarized. (f) Fundamental input mixed polarized and reflected SH output p polarized. (g) Fundamental input mixed polarized and transmitted SH output p polarized. The fit parameters are listed in Tables II and III.

TABLE II. Best-fit parameters for seven-parameter model for SHG at $\lambda = 1.046\ \mu m$ from a C_{60} film.

Nonlinear susceptibility component	Susceptibility (10^{-15} esu)
$\chi_{s,zzz}(q/f) - \gamma$	22.8
$\chi_{s,zzz}(f/v) + \gamma$	−41.7
$\chi_{s,zyy}(q/f) - \gamma$	6.1
$\chi_{s,zyy}(f/v) + \gamma$	−2.9
$\chi_{s,yzy}(q/f)$	3.9
$\chi_{s,yzy}(f/v)$	−4.3
δ'	10.0

TABLE III. Best-fit bulk susceptibilities ($\overleftrightarrow{\chi}^P, \overleftrightarrow{\chi}^Q$) and four-dependent susceptibilities ($\delta, \beta, \gamma, \delta'$) for SHG at $\lambda = 1.064\ \mu m$ from a C_{60} film.

Bulk susceptibility component	Susceptibility (10^{-15} esu)
χ_2^P	−1.3
χ_3^P	−9.2
χ_4^P	1.7
χ_2^Q	5.9
$\chi_3^Q = \chi_4^Q$	−3.3
δ	−16.2
β	4.0
γ	−15.1
δ'	10.0

D.Wilk, D.Johannsmann, C.Stanners and Y.R.Shen, Phys.Rev.B 51, 10057 (1994)

Rotational anisotropy

$$P_i(\Omega) = \gamma\nabla_i(\mathbf{E}\cdot\mathbf{E}) + (\delta-\beta-2\gamma)(\mathbf{E}\cdot\nabla)E_i + \zeta E_i\nabla_i E_i$$

$$\zeta \neq 0$$

The cartesian coordinate axes coincide, in this expression, with the principal crystallographic axes. When estimating the values of the generated fields in different polarization combinations, one needs to transform $\chi_q^{(2)}$ into the laboratory axes.

As a general rule, rotational measurements of the L-th order multipole contribution to the N-th order NLO process of a material with q-fold rotational symmetry can only show anisotropic response if N + L ≥ q.

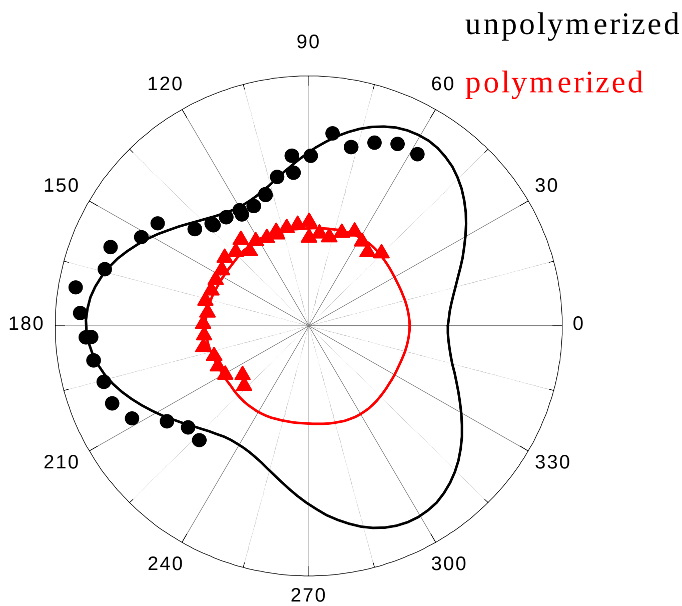
For cubic centrosymmetric materials (m3m- or 432-symmetry), the variation of the SH fields with an arbitrary azimuthal angle can be written as

$$E_p(\Omega) = a + b^{(m)}\cos(m\varphi)$$
$$E_s(\Omega) = c^{(m)}\sin(m\varphi)$$

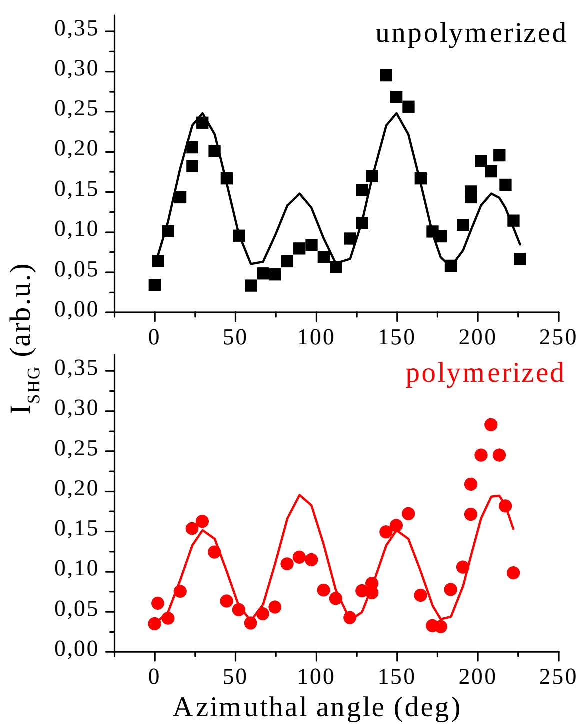
where m = 3 for (111) crystal faces and m = 4 for (001) crystal faces. For a (110) face,

$$E_p(\Omega) = a + b^{(2)}\cos(2\varphi) + b^{(4)}\cos(4\varphi)$$
$$E_s(\Omega) = c^{(2)}\sin(2\varphi) + c^{(4)}\sin(4\varphi)$$

Photopolymerization of a crystalline C_{60} film

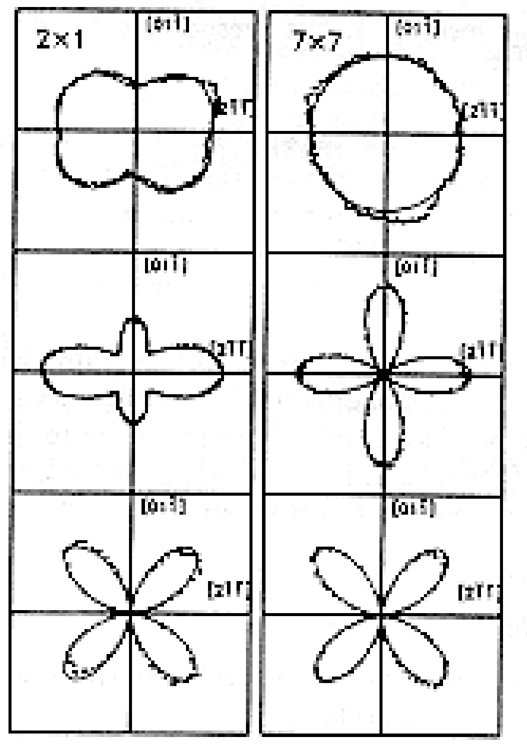


p-p signal



ps signal

Reconstruction of Si(111) surfaces



The polarization dependence for a SH signal associated only with the surface nonlinear susceptibility, for normal incidence:

* Si(111)-7x7:

$I_x(\Omega) = A|\chi^{(2)}_{s,xxx}|^2\cos^2 2\varphi$

$I_y(\Omega) = A|\chi^{(2)}_{s,xxx}|^2\sin^2 2\varphi$

* Si(111)-2x1

$I_x(\Omega) = A|\chi^{(2)}_{s,xxx}\cos^2\varphi + \chi^{(2)}_{s,xyy}\sin^2\varphi|^2$

$I_y(\Omega) = A|\chi^{(2)}_{s,xxx}|^2\sin^2 2\varphi$

T.F.Heinz, M.M.T.Loy and W.A.Thompson, Phys.Rev.Lett. 54, 63 (1985)