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Second-Harmonic Generation in Centro-Symmetric Media

D. Epperlein, B. Dick, and G. Marowsky

Max-Planck-Institut für biophysikalische Chemie, Abteilung Laserphysik, D-3400 Göttingen, Fed. Rep. Germany

G. A. Reider

Institut für Allgemeine Elektrotechnik und Elektronik, Abteilung Quantenelektronik und Lasertechnik, TU Wien, A-1040 Wien, Austria

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Abstract. We have studied the magnetic-dipole and electric-quadrupole contributions to second-harmonic generation (SHG) of centro-symmetric media. It can be shown that the phenomenological parameters α, β, γ can be arranged to form an effective $\tilde{\chi}_s^{(2)}$-tensor, which describes dipole-forbidden SHG as the effect of a surface layer upon excitation with a single plane electromagnetic wave. An experimental technique is proposed allowing a determination of the usually very small γ term due to magnetic-dipole interaction using coherent compensation of its contribution by a coverage with an appropriate dye monolayer.

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Second-harmonic (SH) generation at boundaries and interfaces has been developed into a powerful tool for surface characterization since the pioneering work of Shen and coworkers [1–4]. In particular, surface coverages with effective SH generators such as resonantly excited monolayers of organic dyes have gained increasing scientific interest. Improved experimental detection techniques however, now also allow the observation of small SH signals generated at rather modest laser input energies due to frequency conversion in the substrate material itself. In centrosymmetric media such as glass or fused quartz, SH generation is dipole-forbidden by symmetry reasons. It is the purpose of this contribution to demonstrate both in theory and experiment that SH generation in centrosymmetric media is localized at the surface of these media and hence that the SH process itself can be conveniently described in the format of a surface susceptibility tensor $\tilde{\chi}_s^{(2)}$. Components of this tensor are the phenomenological parameters α, β, γ, which have been introduced in the early studies on SH generation in [5–7]. For the sake of simplicity, we consider an ideal case where the bulk structure of the substrate material extends all the way to the boundary plane. In real cases the inversion symmetry of the bulk is broken in the surface layer and consequently SH generation is allowed in the electric dipole approximation. Following the notation of [4] the discussion of this contribution is limited to the case of a "field discontinuity".

1. Theory

The effects of SH generation, sum- and difference-frequency generation are described by a nonlinear polarization $\mathbf{P}^{(2\omega)}$, which can be derived from second-order time-dependent perturbation theory by considering the interaction of the (classical) external fields with the material system [8, 9]. With $\tilde{\chi}^{(2)}$ denoting the nonlinear susceptibility, $\mathbf{P}^{2\omega}$ can be written as

$$\mathbf{P}^{2\omega} = \tilde{\chi}^{(2)} : \mathbf{E}(\omega)\mathbf{E}(\omega), \quad (1)$$

or in components

$$\mathbf{P}_i^{2\omega} = \sum_{jk} \chi_{ijk} E_j(\omega) E_k(\omega) \quad (ijk = x, y, z). \quad (2)$$

The number of independent tensor components can be considerably reduced by the symmetry operations of the particular process. Using piezoelectric contraction [10], the nonlinear susceptibility of a surface layer $\bar{\chi}_s^{(2)}$ reduces to 3 independent components,

$$\chi_{31}=\chi_{32}, \chi_{33}, \chi_{24}=\chi_{15}. \tag{3}$$

Hence the polarization $\mathbf{P}^{2\omega}$ of a surface layer can be described by the expression:

$$\begin{vmatrix} P_x \\ P_y \\ P_z \end{vmatrix} = \begin{vmatrix} \cdot & \cdot & \cdot & \cdot & \chi_{15} & \cdot \\ \cdot & \cdot & \cdot & \chi_{24} & \cdot & \cdot \\ \chi_{31} & \chi_{32} & \chi_{33} & \cdot & \cdot & \cdot \end{vmatrix} \begin{vmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_zE_y \\ 2E_zE_x \\ 2E_xE_y \end{vmatrix}. \tag{4}$$

Characterization of the nonlinear response of a surface requires the identification of these 3 remaining components by 3 independent measurements [11].

Subsequently we want to describe SH generation in centrosymmetric media with such a tensor $\bar{\chi}_s^{(2)}$. Since the susceptibility $\bar{\chi}^{(2)}$ of (1) is a third-rank tensor of even parity under inversion, $\chi^{(2)}$ vanishes for media with inversion symmetry. In order to account for higher-order contributions to $\mathbf{P}^{2\omega}$ of centrosymmetric media, one introduces the nonlocal expansion [3]

$$\mathbf{P}^{2\omega}=\bar{\bar{\mathbf{Q}}}\vdots\mathbf{E}(\omega)\mathbf{\nabla}\mathbf{E}(\omega) \tag{5}$$

with $\bar{\bar{\mathbf{Q}}}$ the fourth-rank tensor of the multipole terms. With $\nabla_k=\partial/\partial x_k$ Eq. (5) can be written in components

$$P_i^{2\omega}=\sum_{jkl} Q_{ijkl}E_j(\omega)\nabla_k E_l(\omega). \tag{6}$$

Subjecting the tensor Q_{ijkl} to the symmetry conditions of a centrosymmetric medium and considering the rotation invariance of the coordinates x and y results in 4 nonvanishing components [12, 13]:

$$Q_{iiii}, Q_{iijj}, Q_{ijij}, Q_{ijji}. \tag{7}$$

These 4 components are usually denoted by $\alpha, \beta, \gamma, \delta$ in the literature. Since the actual identification is quite different, we adopt here the notation of [5]

$$\begin{aligned} Q_{iiii}&=\alpha, \\ Q_{iijj}&=\beta, \\ Q_{ijij}&=2\gamma, \\ Q_{ijji}&=\delta. \end{aligned} \tag{8}$$

According to [12] there exists the following relation between these parameters:

$$\alpha=\beta+2\gamma+\delta. \tag{9}$$

The multipole contribution to the nonlinear polarization $\mathbf{P}^{2\omega}$ can be expressed with this set of parameters as

$$\mathbf{P}^{2\omega}=\delta(\mathbf{E}\mathbf{\nabla})\mathbf{E}+\beta\mathbf{E}(\mathbf{\nabla}\mathbf{E})+\gamma\mathbf{\nabla}(\mathbf{E}\mathbf{E}), \tag{10}$$

$$P_i^{2\omega}=\Big(\sum_j E_j\nabla_j\Big)\delta E_i+\beta E_i\Big(\sum_j \nabla_j E_j\Big) +2\gamma\sum_j E_j\nabla_i E_j. \tag{11}$$

In order to avoid problems associated with $\nabla\mathbf{E}=0$ in a homogeneous medium such as non-crystalline quartz, we assume for the interfacial layer that the parameters α, β, γ vary continuously from the values in the bulk to the values of the adjacent medium, e.g. air (Fig. 1). In [6] it has been shown that (11) can be split into expressions symmetric and anti-symmetric in the indices i, j in order to subdivide the multipole terms in magnetic-dipole and electric-quadrupole contributions.

Next, we consider SH generation upon excitation with a single, incident electromagnetic wave,

$$\mathbf{E}=\hat{E}\cdot e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}. \tag{12}$$

The ∇-operator works on both the amplitude $\hat{E}=\{\hat{E}_x, \hat{E}_y, \hat{E}_z\}$ and the phase factor

$$\mathbf{\nabla}\mathbf{E}=[(\mathbf{\nabla}\hat{E})-i(\mathbf{k}\hat{E})]\cdot e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}. \tag{13}$$

Assuming lossless propagation in the transparent bulk medium, the first term vanishes in the bulk. It remains, however, at the surface. Consequently surface and bulk contributions will be treated separately.

1.1. Surface Contributions

Figure 1 shows the experimental situation considered: two adjacent centrosymmetric media such as air and

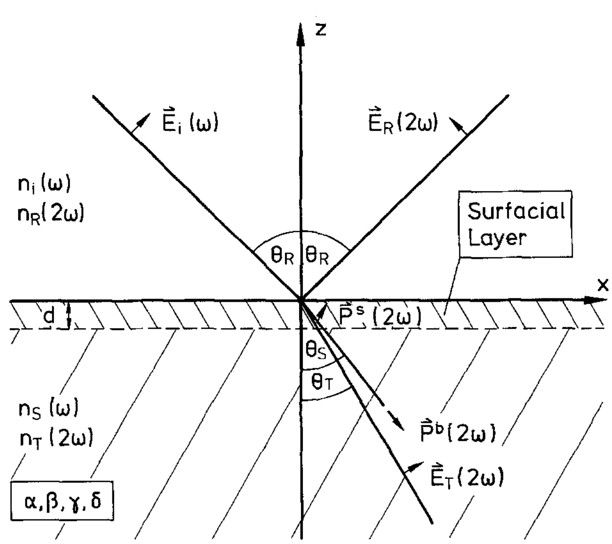

Fig. 1. Optical schematic of incident field $\mathbf{E}_i(\omega)$ and reflected and transmitted SH fields $\mathbf{E}(2\omega)$ produced in an interfacial layer of thickness $d \ll \lambda$

fused quartz. The field discontinuity occurs within an interfacial zone of thickness $d \ll \lambda$ which is characterized by the indices of refraction $n_s(\omega)$ and $n_T(2\omega)$. Hence dispersion guarantees that SH radiation generated in the interfacial zone experiences an angular separation in the bulk of the transparent substrate medium. This medium is also characterized by the parameters α, β, γ, δ phenomenologically describing the nonlinear response of this centrosymmetric medium. In order to obtain an expression for the surface contributions, the polarization $\mathbf{P}^{2\omega}$ will be integrated along the z-direction with $-d \leqq z \leqq 0$. In the limit of $d \to 0$ this corresponds to an integration over a polarization sheet within a $\delta(z)$ environment.

With $\sum_i k_i E_i = 0$ and $\partial \hat{E}_z/\partial_z = \nabla_z \hat{E}_z$ the only nonvanishing component of the product $\nabla\mathbf{E}$, (14) describes the components of the polarization amplitude $\hat{P} = \mathbf{P}^{2\omega} \times \exp(-2i\omega t)$:

$$\hat{P} = \begin{vmatrix} \beta \hat{E}_x \nabla_z \hat{E}_z - 2i\gamma k_x |\hat{E}|^2 \\ \beta \hat{E}_y \nabla_z \hat{E}_z - 2i\gamma k_y |\hat{E}|^2 \\ \alpha \hat{E}_z \nabla_z \hat{E}_z - 2i\gamma k_z |\hat{E}|^2 \end{vmatrix} \cdot e^{-2i\mathbf{k}\cdot\mathbf{r}}. \qquad (14)$$

Integration with $|\mathbf{k}| \cdot |\mathbf{r}| \ll 1$ yields

$$\int_{-d}^{0} \hat{P} dz = \begin{vmatrix} \hat{E}_x \boldsymbol{\beta}[\hat{E}_z(0) - \hat{E}_z(-d)] \\ \hat{E}_y \boldsymbol{\beta}[\hat{E}_z(0) - \hat{E}_z(-d)] \\ \boldsymbol{\alpha}/2[\hat{E}_z^2(0) - \hat{E}_z^2(-d)] \end{vmatrix} - 2i\gamma |\hat{E}|^2 \cdot \begin{vmatrix} k_x \\ k_y \\ k_z \end{vmatrix} \cdot z \Big|_{-d}^{0}. \qquad (15)$$

The average values $\boldsymbol{\alpha} \leqq \alpha$ and $\boldsymbol{\beta} \leqq \beta$ take care of the inhomogeneous character of the assumed interfacial layer. For $d \to 0$ the second term of (15) vanishes and the difference in $\hat{E}_z$ can be expressed with the respective linear susceptibilities

$$\hat{E}_z(0)/\hat{E}_z(-d) = \varepsilon_s/\varepsilon_i. \qquad (16)$$

Subdividing the nonlinear polarization $\mathbf{P}^{2\omega}$ into a bulk contribution $\mathbf{P}^b$ and a surface contribution $\mathbf{P}^s$, the latter can now be expressed as

$$\mathbf{P}^s = \delta(z)\mathbf{Q}^s : \mathbf{E}(\omega)\mathbf{E}(\omega), \qquad (17)$$

$$\mathbf{Q}^s = \begin{vmatrix} \cdot & \cdot & \cdot & \cdot & B & \cdot \\ \cdot & \cdot & \cdot & B & \cdot & \cdot \\ \cdot & \cdot & A & \cdot & \cdot & \cdot \end{vmatrix}, \qquad (18)$$

$$A = \boldsymbol{\alpha}[(\varepsilon_s/\varepsilon_i)^2 - 1]/2, \qquad (19)$$

$$B = \boldsymbol{\beta}[\varepsilon_s/\varepsilon_i) - 1]/2. \qquad (20)$$

Our derivation of the nonlinear surface polarisation $\mathbf{P}^s$ thus essentially considers the field discontinuity between two homogeneous, centrosymmetric media. It should be mentioned that this discontinuity can be partially compensated by matching the refraction index difference between the two adjacent media, as has been demonstrated recently by Guyot-Sionnest and Shen [20]. Their paper indicates also that, in general, multipole effects can be severely masked by structural discontinuities along the surface: the interfacial layer has in its transition regime no longer the symmetry properties of the (centrosymmetric) bulk and thus adds an electric dipole-allowed contribution to the SHG process. The relations for the quantities A and B show the different character of the contributions obtained for the nonlinear polarisation components P_x^s, P_y^s, and P_z^s: the discontinuity in the field component in z direction leads to a weighting factor $(\varepsilon_s/\varepsilon_i)^2$, whereas the usually continuous components P_x^s and P_y^s are only affected by $\varepsilon_s/\varepsilon_i$. The symmetry of the $\bar{\mathbf{Q}}^s$-tensor and the properties of the components A and B will be discussed in detail in connection with an appropriate expression for the γ-terms.

1.2. Bulk Contributions

Again lossless propagation in the dispersive centrosymmetric medium is assumed. With $\nabla_i \hat{E}_i = 0$, we consider only the behavior of the differentiation of the phase factor in (13). However, it should be pointed out that the first term might also yield a contribution if several waves incident from different directions act on the sample. The bulk contribution $\mathbf{P}^b$ is defined by

$$\mathbf{P}^b = 2i\gamma |\mathbf{E}_t|^2 \mathbf{k}_t = i\gamma |\mathbf{E}_t|^2 \cdot \mathbf{k}_s. \qquad (21)$$

The propagation properties of such a longitudinal polarization have been discussed in detail by Bloembergen and Pershan [14]. Although it does not result in a growing, propagating wave within the substrate medium, the polarization $\mathbf{P}^b$ must be treated as in the case of frequency conversion within the bulk of a medium of high nonlinear susceptibility such as KDP. This problem has been discussed in [14] and [Ref. 14, Eqs. (4.5, 8, 13, 14)] apply. In our case the direction of $\mathbf{P}^b$ coincides with the propagation of the fundamental wave $E_t(\omega)$. According to [Ref. 14, Eq. (4.14)] the amplitude $E_T(2\omega)$ depends only on the amplitude of the incident fundamental wave and does not depend on the spatial coordinate for perfect phase matching. In the case of imperfect phase matching, a space-dependent contribution must be added:

$$\mathbf{E}_{\parallel}^T = \frac{4\pi}{\varepsilon_T} \mathbf{P}^b(\Theta_R, \Theta_S, \Theta_T, \ldots). \qquad (22)$$

(The angles Θ_R, Θ_S, Θ_T have been defined in Fig. 1.)

This additional modulation $E_{\parallel}^T$ does not exceed 5% of the space-independent amplitude and will be neglected. In particular, this is justified since differentiation of the phase factor reduces any magnetic-dipole contribution by a factor $k \cdot d \approx 10^{-3}$ as compared to

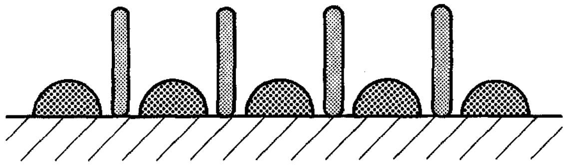

Fig. 2. Idealized model of an effective surface layer responsible for SH generation of centrosymmetric media consisting of a well-oriented structure of rod-like dipoles sensitive to p-polarized excitation derived from electric-quadrupole contributions and a substructure, sensitive to s-polarized excitation due to magnetic-dipole contributions

electric-dipole allowed contributions. Since the SH signal in reflection from a centrosymmetric medium is based upon a single space-independent source term [Ref. 14, Eq. (4.13)], we may consider the total bulk contribution equivalent to the SH contribution of an appropriate (in terms of magnitude and symmetry) surface layer and assume that the nonlinear polarization vanishes in the interior of the medium. A comparison of [Ref. 14, Eq. (4.14)] and computations in [3], where the picture of a $\delta(z)$ polarization sheet has been dealt with in detail, yields for $\mathbf{P}^b$ the expression

$$P^b = \delta(z)\mathbf{Q}^b : \mathbf{E}_t\mathbf{E}_t \tag{23}$$

with

$$Q^b = \left| \begin{matrix} . & . & . & . & . & . \\ . & . & . & . & . & . \\ \frac{\varepsilon_M}{\varepsilon_T}\gamma & \frac{\varepsilon_M}{\varepsilon_T}\gamma & \frac{\varepsilon_M}{\varepsilon_T}\gamma & . & . & . \end{matrix} \right| . \tag{24}$$

ε_M denotes the dielectric constant of the interfacial layer. It is again convenient to introduce an effective value Γ

$$\Gamma = \gamma_{\varepsilon_M/\varepsilon_T} \tag{25}$$

1.3. The Total Polarization $\mathbf{P}^{2\omega}$

The previously discussed contributions $\mathbf{P}^s$ and $\mathbf{P}^b$ can be added to yield

$$\mathbf{P}^{2\omega} = \mathbf{P}^s + \mathbf{P}^b = \delta(z)\bar{\mathbf{Q}} : \mathbf{E}_t\mathbf{E}_t \tag{26}$$

with

$$\bar{\mathbf{Q}} = \left| \begin{matrix} . & . & . & . & B & . \\ . & . & . & B & . & . \\ \Gamma & \Gamma & (\Gamma + A) & . & . & . \end{matrix} \right| . \tag{27}$$

The components of this tensor exhibit the properties of a surface susceptibility tensor $\bar{\chi}_s^{(2)}$ as already discussed with the identities $\chi_{31} \equiv \chi_{32}$, $\chi_{24} \equiv \chi_{15}$ and (usually) $\chi_{33} \neq \chi_{31}$, χ_{15}. The format of the $\bar{\mathbf{Q}}$-tensor of (27) suggests the idealized picture of Fig. 2. SH generation in centrosymmetric media can be described in terms of a well-oriented dipole layer [coefficients A and B in (27)] derived from electric quadrupole contributions, preferentially sensitive to p-polarized excitation. In addition, a weak SH signal which is based upon magnetic dipole contributions [coefficient Γ in (27)] should be observable under s-polarized excitation and p-oriented detection. The coefficients A and B disappear under perfect phase matching, $\varepsilon_s = \varepsilon_i$, whereas the bulk contribution Γ is always present. Reference [15] discusses in detail the effect on optical properties of centrosymmetric media due to multipoles, which cancel each other in the bulk and lead to surface currents and an electric dipole layer.

2. Experimental Results

As a result of the preceding considerations, it can be summarized that SH generation in centrosymmetric media is due to an effective surface layer of well-defined components of a $\bar{\chi}_s^{(2)}$-tensor. Figure 3, taken from [16], shows the result of a simple, preliminary experiment, which in spite of the low spatial resolution, seems to demonstrate the localization of the SH source at the

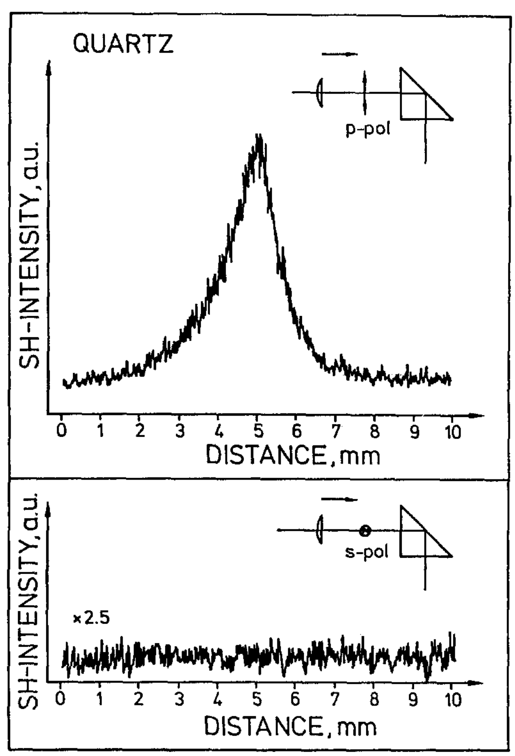

Fig. 3. SH signal of quartz in total internal reflexion under p- and s-polarized excitation

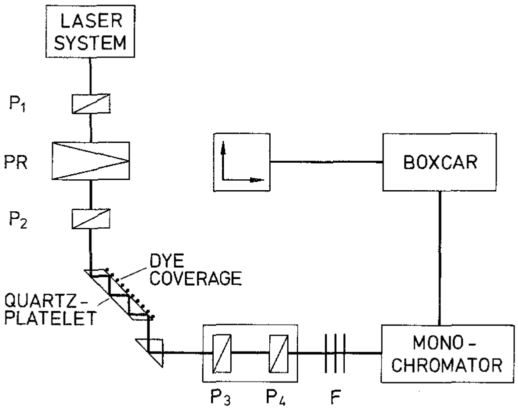

Fig. 4. Experimental setup for polarization-sensitive excitation and detection of the SH radiation produced in a quartz-platelet. The dye coverage is only added for compensation of the small SH contribution under s excitation ($\varphi=90°$)

surface of the quartz prism and which also shows the unsuccessful excitation of SH radiation under s-polarized fundamental radiation. In an effort to observe the very weak signals upon s-excitation we have built up an experimental setup which creates 20 successive reflexions in a quartz platelet of 1 mm thickness of etalon quality. As shown in Fig. 4, the polarization of the fundamental was carefully kept under control by means of polarizers P_1 and P_2 before and after the polarization rotation unit. Polarization-sensitive detection of the SH light could be performed by means of the polarizers P_3 and P_4. Although s-excitation and p-analysis considerably reduced straylight problems in the detection system, the final signal-to-noise ratio could be improved by unpolarized detection. Figure 5 shows a polar-diagram of the total SH signal

$$S^{2\omega}=(P_{\perp}^{2\omega})^2+(P_{\parallel}^{2\omega})^2 \tag{28}$$

versus the polarization angle φ. Following the notation of [14], $P_{\perp}^{2\omega}$ denotes the nonlinear polarization perpendicular to the plane of incidence ($P_{\perp}^{2\omega}=P_y$) and $P_{\parallel}^{2\omega}$ the polarization in the plane of incidence $P_{\parallel}^{2\omega}=\{P_x, P_z\}$. The solid curve represents a least-square fit to the function

$$S^{2\omega}=a^2\cos^4\varphi+b^2\sin^4\varphi+(2ab+c)\sin^2\varphi\cos^2\varphi \tag{29}$$

with $b^2/a^2=0{,}02$ and c obtained from the fitting routine. The function $S^{2\omega}=S^{2\omega}(\varphi)$ is an immediate consequence of the tensor $\tilde{\chi}_s^{(2)}$ and the field components

$$\begin{aligned} E_x &= E\cdot f_x\cdot\cos\varphi\cos\alpha\,,\\ E_y &= E\cdot f_y\cdot\sin\varphi\,,\\ E_z &= E\cdot f_z\cdot\cos\varphi\sin\alpha\,. \end{aligned} \tag{30}$$

The coefficients $\{f_x, f_y, f_z\}$ denote the linear Fresnel factors [11, 17] in order to characterize the effective fundamental field inside quartz. For an angle of incidence of 45° and nonlinear Fresnel factors $\{\tilde{f}_x, \tilde{f}_y, \tilde{f}_z\}$ as defined by [Ref. 11, Eq. (13)] the quantities a, b, and c result in the following expressions

$$\begin{aligned} 2a &= 2\tilde{f}_x\chi_{15}f_xf_z+\tilde{f}_z(\chi_{31}f_x^2+\chi_{33}f_z^2)\,,\\ b &= \tilde{f}_z\chi_{31}f_y^2\,,\\ c &= 2(\tilde{f}_y\chi_{15}f_yf_z)^2\,. \end{aligned} \tag{31}$$

Evaluation of these expressions permits, in principle, to obtain numerical values for the actual tensor components and a comparison with the values for α, β, and γ known from literature. However, since multiple total internal reflexion is not a well-defined geometry, we limit the evaluation to

$$\chi_{31}\leqq 0.3\cdot\chi_{33} \tag{32}$$

under the additional assumption

$$\tilde{f}_z\chi_{33}f_z^2 \ll \tilde{f}_x\chi_{15}f_xf_z\,. \tag{33}$$

In fact, the quantity χ_{31} might be even smaller by one order of magnitude, since surface layers of dyes of known $\tilde{\chi}_s^{(2)}$ show a considerable enhancement of the s-excited SH signal in total internal reflexion as compared to Fresnel reflection [18]. In order to decide whether the small SH contribution at $\varphi=90°$ is really an effect due to χ_{31} and enhanced by the multiple total internal reflexion geometry, the quartz substrate was covered on both sides with the dye 4-dimethylaminopyridine (4-DAP). The carefully cleaned etalon was drawn (at constant speed) out of different 4-DAP solutions in propanole, within a concentration range from 10^{-2} to 10^{-7} moles/liter. Partial and at high concentrations complete surface coverage did not affect the SH signal under p-excitation ($\varphi=0$, cf. Fig. 5). However, the s-excited signal showed the surprising behavior depicted in Fig. 6. We interpret the complete disappearance of the s-excited SH signal at an original concentration of 10^{-5} moles/liter as an

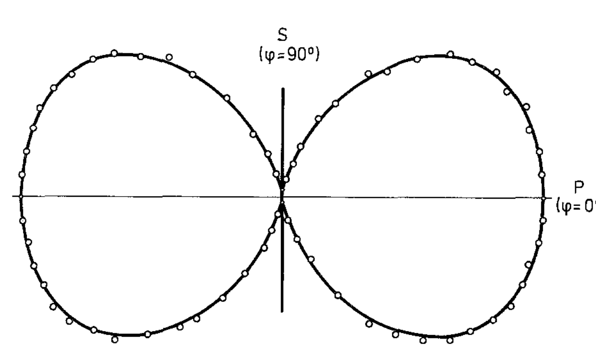

Fig. 5. Unpolarized, total SH signal versus polarization angle φ

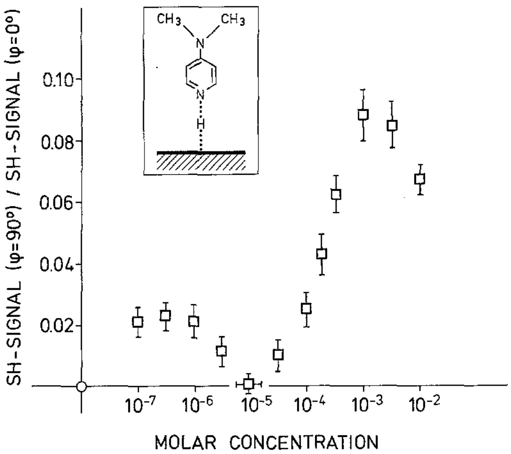

Fig. 6. Dependence of the small SH signal under $\varphi=90°$ (s polarized excitation) versus molar concentration of the dye 4-DAP. Insert shows presumable position of the dye 4-DAP at quartz surface

indication of coherent compensation of the corresponding tensor components. This implies the relation

$$\Gamma_{eff}(\text{Quartz}) = -|N \cdot \chi_{31}(\text{4-DAP})|, \quad (34)$$

with N the surface coverage density obtained from the 10^{-5} molar solution of 4-DAP and Γ_{eff} (quartz) denoting the quantity Γ due to quartz as observed under the particular geometry. The idea of an addition of different tensor components due to dipole-allowed contributions of a dye monolayer and higher order multipole contributions from the bulk has already been discussed in [16]. The finding that an external coverage of the quartz surface compensates for its bulk contribution appears to us as clear evidence that the effect of this weak magnetic dipole contribution is localized at the surface of the centrosymmetric medium. In addition, this nulling-method offers the unique possibility of an unambiguous determination of the sign of the 3 nonvanishing $\chi_s^{(2)}$ components by balancing it against a substrate or another SH-active medium of known susceptibility. So far, a determination of the absolute sign of a particular $\chi_s^{(2)}$-component is rather tedious, since all SH intensities are proportional to the square of the respective polarization.

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