Uniqueness of wave-plate measurements in determining the tensor components of second-order surface nonlinearities

Jeffery J. Maki, Martti Kauranen, Thierry Verbiest, and André Persoons
Laboratory of Chemical and Biological Dynamics and Center for Research on Molecular Electronics and Photonics, University of Leuven, Celestijnenlaan 200D, B-3001 Heverlee, Belgium

(Received 20 December 1995; revised manuscript received 28 August 1996)

The relative amplitude and phase of the components of the second-order susceptibility tensors for second-harmonic generation from a chiral surface can be determined by making measurements of the second-harmonic intensity. The intensity of the p and s components of the reflected or transmitted second-harmonic wave must be measured, but the measurements need not be calibrated nor even be on the same relative intensity scale. However, these intensity measurements must be made as functions of the polarization state of the fundamental radiation. We prove that it is sufficient to make these measurements at a single angle of incidence provided that a wave plate of any retardation other than half wave is used to manipulate the polarization state of the fundamental radiation. Quarter-wave retardation is a good choice. We derive explicit formulas to determine the susceptibility components from the parameters found to describe the intensity measurements, where the electric dipole approximation is made in the description of the nonlinearity. [S0163-1829(97)03908-8]

I. INTRODUCTION

Chiral molecules have received attention lately as potential nonlinear-optical materials owing to the rich nature of their optical response.[1,2] In linear optics, chirality of a material system is exhibited by optical activity and is typically quantified through measurements of optical rotatory dispersion or circular dichroism.[3] A nonlinear-optical technique has been discovered for detecting molecular chirality.[4] The efficiency of second-harmonic generation from a surface composed of chiral molecules depends upon the handedness of the circularly polarized fundamental radiation used to drive the nonlinearity. The difference in the efficiency is known as second-harmonic generation circular dichroism/difference (SHG-CD),[4,5] and the sign of the difference depends upon the particular enantiomer composing the chiral surface.

SHG-CD was first used to demonstrate nonlinear optical activity of chiral surfaces,[2,4–15] but other methods have been discovered. One is second-harmonic generation linear difference (SHG-LD),[16–18] which is where the efficiency of the harmonic generation changes between two different linear-polarization states for the fundamental radiation. Another is second-harmonic generation optical rotatory dispersion[11,19,20] (SHG-ORD) or polarization-azimuth rotation.[5] Still others are possible,[5] but all require isotropic surfaces such that these effects can be used to detect chirality.[15,21] An experiment has already demonstrated that nonlinear optical activity can occur for an anisotropic achiral surface, where the molecules composing the surface are neither chiral nor even arranged on the surface with chiral symmetry properties.[21]

Regardless of the symmetry type of the nonlinear surface layer, the second-harmonic photon can always be thought of as resulting from the annihilation of two p-polarized fundamental photons, two s-polarized fundamental photons, or one p-polarized fundamental photon with one s-polarized fundamental photon. An equation describing this is

$$I(2\omega)=|fE_{I_p}^2(\omega)+gE_{I_s}^2(\omega)+hE_{I_p}(\omega)E_{I_s}(\omega)|^2, \quad (1)$$

where the expansion parameters f, g, and h are complex valued and $E_{I_p}(\omega)$ and $E_{I_s}(\omega)$ are, respectively, the p- and s-polarized components of the complex-valued amplitudes of the fundamental electric field incident upon the nonlinear surface. We note that some of the expansion parameters may vanish for some surfaces, but there are no more than these three parameters. Also, Eq. (1) shows that the second-harmonic signal does not depend upon the overall phase of the parameters, but only on the relative phase among them. The expansion parameters are linear functions of the components of the second-order susceptibility tensors. One might consider f, g, and h to be susceptibilities,[15] but in a p-s coordinate system rather than in Cartesian coordinates; however, these parameters will change in value with changes in the angle of incidence, so they are not purely material response parameters as susceptibilities are usually defined. Nevertheless, f, g, and h are the parameters that can be measured most directly in an experiment.

In earlier measurements of SHG-CD of chiral isotropic surfaces,[2,10,22,23] a quarter-wave plate was not only positioned to yield left- and right-hand circularly polarized fundamental radiation, but was varied continuously over the whole range of possible wave-plate angles. By fitting Eq. (1) to the measured response curve, the amplitude and relative phase of the parameters f, g, and h were determined. In related experiments, achiral isotropic surfaces were studied using a half-wave plate,[24,25] but a limitation of this method is the fact that the parameters cannot be determined uniquely (even to an overall scaling of phase) unless measurements are made at more than one angle of incidence.[25] Such a limitation does not occur when using a quarter-wave plate. This advantage of using a quarter-over a half-wave plate has recently been exploited in a study of an achiral isotropic surface[26] and could be exploited in studying anisotropic surfaces.[21]

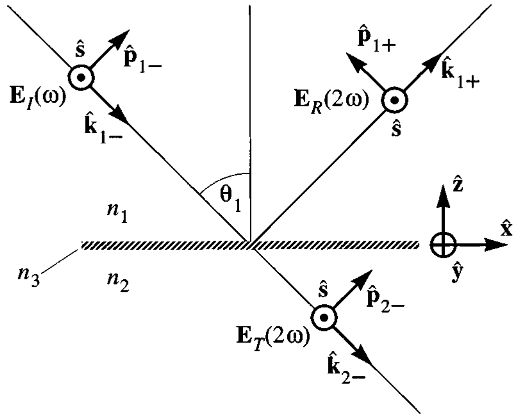

FIG. 1. Typical geometry of surface second-harmonic generation showing the unit vectors for the incident fundamental wave, and the reflected and transmitted second-harmonic waves. The hatched line indicates the thin nonlinear surface layer. The circles with dots or crosses indicate vectors out of or into the drawing, respectively.

In this paper, we extend the theoretical results of Ref. 14 to form a theoretical basis for methods already used in Refs. 2, 10, 22, and 23. In Sec. II we examine the action of a wave plate in manipulating the polarization state of the fundamental radiation and we prove that the parameters f, g, and h can be determined uniquely (within an overall phase ambiguity) from measurements of the surface second-harmonic intensity. The results also prove that measurements at only a single angle of incidence are required providing that a wave plate of any retardation other than half wave is used. This is a general result applicable to many surface types. In Sec. III we also illustrate the information content and utility in measuring the parameters by giving formulas relating the components of the second-order susceptibility tensor directly to the parameters for a chiral isotropic surface. These formulas are derived under the assumption that the nonlinearity of the surface can be described within the electric dipole approximation. In Sec. IV we summarize the results of the paper and discuss their applicability to future experiments.

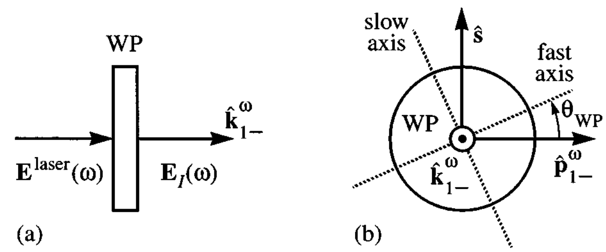

FIG. 2. (a) Preparation of the polarization state of the incident fundamental electromagnetic field by propagation of a p-polarized laser beam (i.e., $\mathbf{E}^{\text{laser}}=E^{\text{laser}}\hat{\mathbf{p}}_{1-}^{\omega}$) through a wave plate. (b) Definition of the wave-plate angle θ_{WP} with respect to the $\hat{\mathbf{p}}_{1-}^{\omega}$ and $\hat{\mathbf{s}}$ directions, where $\hat{\mathbf{k}}_{1-}^{\omega}$ is the propagation direction of the laser beam. The circle with a dot indicates a vector out of the drawing.

II. UNIQUENESS OF THE EXPANSION PARAMETERS

We examine to what extent the expansion parameters f, g, and h can be determined assuming the use of a wave plate to manipulate the polarization state of the fundamental radiation. The fundamental electric field

$$\mathbf{E}_I(\mathbf{r})=[E_{I_p}(\omega)\hat{\mathbf{p}}_{1-}^{\omega}+E_{I_s}(\omega)\hat{\mathbf{s}}]\exp(i\mathbf{k}_{1-}^{\omega}\cdot\mathbf{r}) \tag{2}$$

incident on the surface (see Fig. 1) after traversing a wave plate (see Fig. 2) is related to the electric field

$$\mathbf{E}^{\text{laser}}(\mathbf{r})=[E_p^{\text{laser}}(\omega)\hat{\mathbf{p}}_{1-}^{\omega}+E_s^{\text{laser}}(\omega)\hat{\mathbf{s}}]\exp(i\mathbf{k}_{1-}^{\omega}\cdot\mathbf{r}) \tag{3}$$

of the laser by

$$\begin{bmatrix} E_{I_p}(\omega) \\ E_{I_s}(\omega) \end{bmatrix}=T_{\text{WP}}(\delta)\begin{bmatrix} E_p^{\text{laser}}(\omega) \\ E_s^{\text{laser}}(\omega) \end{bmatrix}. \tag{4}$$

The Jones matrix for a wave plate of linear retardation δ is[27]

$$T_{\text{WP}}(\delta)=\begin{bmatrix} \cos\delta-i\ \sin\delta\ \cos2\theta_{\text{WP}} & -i\ \sin\delta\ \sin2\theta_{\text{WP}} \\ -i\ \sin\delta\ \sin2\theta_{\text{WP}} & \cos\delta+i\ \sin\delta\ \cos2\theta_{\text{WP}} \end{bmatrix}, \tag{5}$$

where $\delta=\pi/4$ for a quarter-wave plate and $\delta=\pi/2$ for a half-wave plate. We shall consider the situation where the laser is p polarized only (i.e., $E_s^{\text{laser}}=0$). Note that, for this case of input polarization to a quarter-wave plate, right- and left-hand circularly polarized light are produced for $\theta_{\text{WP}}=\pi/4$ and $-\pi/4$, respectively.

The completely general expressions $f=(f_1+if_2)e^{i\varphi}$, $g=(g_1+ig_2)e^{i\varphi}$, and $h=h_1e^{i\varphi}$ with $h_1>0$ make the overall phase of the parameters explicit. Equation (1) gives the second-harmonic intensity, after substituting the expressions for $E_{I_p}(\omega)$ and $E_{I_s}(\omega)$ from Eq. (4), to be

$$\begin{aligned} I(2\omega)={}&\tfrac{1}{4}[(f_1+g_1)\sin^2\delta-2\,f_1\cos^2\delta-4f_2\cos\delta\ \sin\delta\ \cos2\theta_{\text{WP}}+(f_1-g_1)\sin^2\delta\ \cos4\theta_{\text{WP}}+h_1\sin^2\delta\ \sin4\theta_{\text{WP}}]^2+\tfrac{1}{4}[(f_2\\ &+g_2)\sin^2\delta-2\,f_2\cos^2\delta+4f_1\cos\delta\ \sin\delta\ \cos2\theta_{\text{WP}}+(f_2-g_2)\sin^2\delta\ \cos4\theta_{\text{WP}}+2h_1\cos\delta\ \sin\delta\ \sin2\theta_{\text{WP}}]^2, \end{aligned} \tag{6}$$

where the expansion parameters f_1, f_2, g_1, g_2, and h_1 have been scaled uniformly to remove the explicit dependence on the intensity of the fundamental field. Equation (6) shows that measurement of the second-harmonic intensity does not provide any information about the absolute phase φ of the parameters f, g, and h. However, the amplitude and relative phase of f, g, and h may be determined providing the real-valued parameters f_1, f_2, g_1, g_2, and h_1 can be determined uniquely.

For a half-wave plate, Eq. (6) reduces to

$$I(2\omega)=\frac{[f_1+g_1+(f_1-g_1)\cos4\theta_{\mathrm{WP}}+h_1\sin4\theta_{\mathrm{WP}}]^2}{4}+\frac{[f_2+g_2+(f_2-g_2)\cos4\theta_{\mathrm{WP}}]^2}{4}. \tag{7}$$

Equation (7) is unchanged when the signs of the two parameters f_2 and g_2 are transformed using $f_2\rightarrow -f_2$ and $g_2\rightarrow -g_2$. Hence these two parameters cannot be determined uniquely when using a half-wave plate to manipulate the polarization state of the fundamental radiation, which shows the need to prove that the parameters can be determined uniquely for other cases of retardation δ.

Equation (6) can be expanded out and written as a Fourier series. The result is

$$I(2\omega)=a_0+\sum_{m=1}^{4}[a_m\cos(2m\theta_{\mathrm{WP}})+b_m\sin(2m\theta_{\mathrm{WP}})], \tag{8}$$

where the coefficients are

$$a_0=(f_1^2+f_2^2)\cos^2\delta-(f_1g_1+f_2g_2-\tfrac{1}{2}h_1^2)\cos^2\delta\,\sin^2\delta+\tfrac{1}{8}[3(f_1^2+f_2^2+g_1^2+g_2^2)+h_1^2+2(f_1g_1+f_2g_2)]\sin^4\delta, \tag{9a}$$

$$a_1=(f_1g_2-f_2g_1)\cos\delta\,\sin^3\delta, \tag{9b}$$

$$a_2=(f_1^2+f_2^2-\tfrac{1}{2}h_1^2+f_1g_1+f_2g_2)\sin^2\delta\,\cos^2\delta+\tfrac{1}{2}(f_1^2+f_2^2-g_1^2-g_2^2)\sin^4\delta, \tag{9c}$$

$$a_3=(f_2g_1-f_1g_2)\sin^3\delta\,\cos\delta, \tag{9d}$$

$$a_4=\tfrac{1}{8}(f_1^2+f_2^2+g_1^2+g_2^2-h_1^2-2f_1g_1-2f_2g_2)\sin^4\delta, \tag{9e}$$

$$b_1=-\tfrac{1}{2}f_2h_1(\cos\delta\,\sin^3\delta+4\cos^3\delta\,\sin\delta)+\tfrac{3}{2}g_2h_1\cos\delta\,\sin^3\delta, \tag{10a}$$

$$b_2=\tfrac{1}{2}f_1h_1\sin^2\delta(\sin^2\delta+2\cos^2\delta)+\tfrac{1}{2}g_1h_1\sin^4\delta, \tag{10b}$$

$$b_3=-\tfrac{1}{2}(f_2+g_2)h_1\cos\delta\,\sin^3\delta, \tag{10c}$$

$$b_4=\tfrac{1}{4}(f_1-g_1)h_1\sin^4\delta. \tag{10d}$$

The values of Fourier coefficients can always be determined uniquely. By showing that only a single solution set exists that relates the parameters f_1, f_2, g_1, g_2, and h_1 to the Fourier coefficients a_m and b_m, the uniqueness of the parameters is proven.

The general case of retardation is where $\sin\delta\neq0$, and $\cos\delta\neq0$, which includes the case of a quarter-wave plate, but not a half-wave plate. Equations (10) give

$$f_1=\frac{b_2+2b_4}{h_1\sin^2\delta}, \tag{11a}$$

$$f_2=\frac{-b_1-3b_3}{2h_1\sin\delta\,\cos\delta}, \tag{11b}$$

$$g_1=\frac{b_2+2b_4}{h_1\sin^2\delta}-\frac{4b_4}{h_1\sin^4\delta}, \tag{11c}$$

$$g_2=\frac{b_1+3b_3}{2h_1\sin\delta\,\cos\delta}-\frac{2b_3}{h_1\cos\delta\,\sin^3\delta}. \tag{11d}$$

At this stage, we see that f_1, f_2, g_1, and g_2 can be determined uniquely providing that h_1 can be determined uniquely. The substitution of Eqs. (11) into the expressions for the Fourier coefficients a_m [i.e., Eqs. (9)] gives five equally valid equations for h_1. That only a single solution for h_1 exists for one of these five equations will prove that h_1 can be determined uniquely. Equation (9b) has the single solution

$$h_1=\left[\frac{(b_1b_2+b_2b_3-4b_3b_4)-(2b_1b_4+2b_2b_3+10b_3b_4)\cot^2\delta}{a_1}\right]^{1/2}, \tag{12}$$

since only the positive square root is to be taken under the initial assumption that $h_1>0$. A single solution for h_1 thus proves that all of the parameters can be determined uniquely.

Later we shall need to consider a situation in which g vanishes. In this case, we get

$$f_1=\frac{4b_4}{h_1\sin^4\delta}, \tag{13a}$$

$$f_2=\frac{-2b_3}{h_1\sin^3\delta\,\cos\delta}, \tag{13b}$$

$$h_1=2\left[\frac{a_0\,\sin^4\delta-a_4(8\cos^2\delta+3\sin^4\delta)}{\sin^4\delta(3+\cos2\delta)}\right]^{1/2}. \tag{13c}$$

A single solution in terms of the Fourier coefficients is found and therefore f and h can be determined uniquely even when g is zero.

Another possible situation is that all of the parameters f, g, and h are real valued. In this case, Eqs. (11a) and (11c) are still valid and a single solution

$$h_1=\csc^2\delta\left[\frac{2}{4a_4\cos^2\delta-a_2\sin^2\delta}\right]^{1/2}[b_4^2(4\cos^6\delta+16\cos^4\delta\sin^2\delta+8\cos^2\delta\sin^4\delta)-b_2^2\cos^2\delta\sin^4\delta+b_2b_4(2\cos^4\delta\sin^2\delta-4\cos^2\delta\sin^4\delta-2\sin^6\delta)]^{1/2} \tag{14}$$

is found, which proves the parameters in this limit can be determined uniquely.

For a half-wave plate, Eqs. (9) and (10) give

$$f_1=\frac{b_2+2b_4}{h_1}, \tag{15a}$$

$$g_1=\frac{b_2-2b_4}{h_1}, \tag{15b}$$

$$f_2=\pm\frac{2[h_1^2(a_0-a_2+a_4)-(b_2-2b_4)^2]^{1/2}}{h_1[2b_2^2-8b_4^2+h_1^2(1-2a_0+6a_4)]}\times[(b_2+2b_4)^2-h_1^2(a_0+a_2+a_4)]. \tag{15c}$$

$$g_2=\pm\frac{[h_1^2(a_0-a_2+a_4)-(b_2-2b_4)^2]^{1/2}}{h_1}, \tag{15d}$$

$$h_1^6-4(a_0-3a_4)h_1^4+4(a_2^2+8a_4^2-8a_0a_4+b_2^2-4b_4^2)h_1^2+32(2a_0b_4^2-a_2b_2b_4+a_4b_2^2-2a_4b_4^2)=0, \tag{15e}$$

where the upper or lower signs among the equations must be taken together when forming a given solution set. Equation (15e) has either one or two positive, real-valued solutions for h_1. Because there are two solutions for f_2 and g_2 for a particular value of h_1, there can be up to four different solution sets for the parameters, but there is always a minimum of two. Therefore there is no unique set of parameters that describe the second-harmonic signal. In summary, a half-wave plate can never be used to determine the expansion parameters uniquely from a single angle-of-incidence measurement, but a wave plate of any other retardation can, which includes a quarter-wave plate.

III. SUSCEPTIBILITY-TENSOR COMPONENTS

General expressions for the expansion parameters f, g, and h have already been derived using the general formalism of Sipe[28] and are given by Eqs. (38) of Ref. 14. These equations and measurements of the parameters provide one with the information required to determine the components of the second-order susceptibility tensors. One could determine the calibrated parameters f_1, f_2, g_1, g_2, and h_1 from calibrated measurements of the second-harmonic intensity made using the quarter-wave-plate technique, but that is not necessary in order to find only the relative amplitude and phase of the susceptibility components. All one needs to find is the relative parameters $f^{\rm rel}=(f_1+if_2)/h_1$, $g^{\rm rel}=(g_1+ig_2)/h_1$, and $h^{\rm rel}=1$. The true calibrated amplitude parameter can then be related to these relative parameters by

$$f_{R_j/T_j}=q_{R_j/T_j}f^{\rm rel}_{R_j/T_j}, \tag{16a}$$

$$g_{R_j/T_j}=q_{R_j/T_j}g^{\rm rel}_{R_j/T_j}, \tag{16b}$$

$$h_{R_j/T_j}=q_{R_j/T_j}, \tag{16c}$$

where j again equals either p or s and q_{R_j/T_j} are unknown constants of proportionality. After substituting Eqs. (16) into Eqs. (38) of Ref. 14 and taking the limit of only electric dipole response (i.e., χ^{eem} and χ^{mee} are zero), the resulting equations can be solved directly. We scale the absolute phase and amplitude of the susceptibility components such that $\chi^{eee}_{xxz}=1$ and the remaining nonvanishing independent components are

$$\chi^{eee}_{zzz}=\pm 2\,f^{\rm rel}_{R_s/T_s}f^{\rm rel}_{R_p/T_p}\left(\frac{t^{\omega}_{s13}}{1-r^{\omega}_{s31}r^{\omega}_{s32}}\right)^2\left(\frac{1-r^{\omega}_{p31}r^{\omega}_{p32}}{t^{\omega}_{p13}}\right)^2\frac{[1+r^{\omega}_{s32}]^2}{[1+r^{\omega}_{p32}][1-r^{\omega}_{p32}]}\sec\theta^{\omega}_3\csc^{\omega}_3\frac{1-r^{2\omega}_{p3i}}{1+r^{2\omega}_{p3i}}\cot\theta^{2\omega}_3 \mp 2\,f^{\rm rel}_{R_s/T_s}g^{\rm rel}_{R_p/T_p}\frac{1-r^{\omega}_{p32}}{1+r^{\omega}_{p32}}\cot\theta^{\omega}_3\frac{1-r^{2\omega}_{p3i}}{1+r^{2\omega}_{p3i}}\cot\theta^{2\omega}_3\pm 2\frac{1-r^{\omega}_{p32}}{1+r^{\omega}_{p32}}\cot\theta^{\omega}_3\frac{1-r^{2\omega}_{p3i}}{1+r^{2\omega}_{p3i}}\cot\theta^{2\omega}_3, \tag{17a}$$

$$\chi^{eee}_{zxx}=\pm 2\,f^{\rm rel}_{R_s/T_s}g^{\rm rel}_{R_p/T_p}\frac{1+r^{\omega}_{p32}}{1-r^{\omega}_{p32}}\tan\theta^{\omega}_3\frac{1-r^{2\omega}_{p3i}}{1+r^{2\omega}_{p3i}}\cot\theta^{2\omega}_3, \tag{17b}$$

$$\chi^{eee}_{xyz}=f^{\rm rel}_{R_s/T_s}\frac{t^{\omega}_{s13}}{1-r^{\omega}_{s31}r^{\omega}_{s32}}\frac{1-r^{\omega}_{p31}r^{\omega}_{p32}}{t^{\omega}_{p13}}\frac{1+r^{\omega}_{s32}}{1-r^{\omega}_{p32}}\sec\theta^{\omega}_3, \tag{17c}$$

where $i=2$ and the upper sign is valid or $i=1$ and the lower sign is valid for the susceptibility components determined using the reflected or transmitted waves, respectively. The quantities r and t represent the Fresnel amplitude reflectivity and transmission coefficients, respectively, of either the p- or s-polarized waves as indicated. The angle θ_3 with respect to the surface normal for which a wave vector propagates within the nonlinear surface layer is related to the angle of incidence θ_1 by Snell's law. The superscripts ω or 2ω indicate whether a quantity is to be computed at the fundamental or second-harmonic frequencies, respectively. The precise definitions of all quantities can be found in Ref. 14. Note that g_{R_s/T_s} is predicted to be zero for only electric dipole response and that in Sec. II it was proven f_{R_s/T_s} and h_{R_s/T_s} can still be determined uniquely even if g_{R_s/T_s} vanishes.

Equations (17) represent a very useful means of determining the susceptibility components in the limit of only electric dipole response. The key feature of the experimental method is that each intensity measurement can be made using a different arbitrary intensity scale. The p- and s-polarized components of the second-harmonic intensity do not even have to be measured on the same relative intensity scale. In addition, the susceptibility components can be determined from the expansion parameters measured using either the reflected or transmitted second-harmonic intensity. Both schemes could be used to check for self-consistency in the determination of the susceptibility components.

The susceptibility component χ_{xyz}^{eee} vanishes when there is no chirality for an isotropic surface. Thus the coupling between Eqs. (38) of Ref. 14 for the p- and s-polarized components of the expansion parameters is lost and the solutions given by Eqs. (17) would not be valid. Solutions for the susceptibility components of an achiral surface can be found, though, by making the additional measurement of the scaling factor between the p- and s-polarized components of the expansion parameters.[26]

IV. CONCLUSIONS

A method for determining the relative amplitude and phase of the components of the second-order susceptibility tensors for a chiral surface has been developed. The method makes use of the information gained from studying the process of surface SHG as the polarization state of the fundamental radiation is varied. It is found that a quarter-wave plate is a good choice to use as a polarization manipulating element for the fundamental radiation, but a half-wave plate is not a good choice. The use of a quarter-wave plate allows for the determination of the various parameters describing the strength of SHG arising from the annihilation of two p-polarized photons, two s-polarized photons, or one p-polarized photon with one s-polarized photon. Explicit formulas are given for calculating the susceptibility components in Cartesian coordinates from the measured values of the parameters in a given p-s coordinate system. An overall amplitude and phase ambiguity remains in the determination of the susceptibility components. This problem could be solved, however, by using the well-known reference-sample interferometric technique to measure the absolute magnitude and phase of one of the susceptibility components.[29]

Equations (17) include all the effects of linear-optical Fresnel reflection and transmission. They are applicable for any angle of incidence including those where total internal reflection occurs. We find that one may determine the susceptibility components from measuring the p- and s-polarized components of the second-harmonic wave in just one direction. The use of the reflected or transmitted directions should give the same relative values for the susceptibility components. Any discrepancy would suggest that the material response cannot be described either as an optically thin film or within the electric dipole approximation.

In any future experiments, the parameters f_1, f_2, g_1, g_2, and h_1 appearing in Eq. (6) must be determined first. Because Eq. (6) is a nonlinear functional of the parameters, a nonlinear algorithm must be used to fit a data curve for the second-harmonic intensity measured as a function of the continuous variation of the wave-plate angle θ_{WP}. Another approach would be to fit the data to the Fourier series Eq. (8) (which requires only a linear fitting algorithm) and then to use Eqs. (11) and (12) to compute the parameters f_1, f_2, g_1, g_2, and h_1 from the Fourier-coefficient data. A somewhat similar approach of using Fourier methods to determine the parameters has already been used, but in the study of achiral surfaces.[25,26] The use of Eq. (6) and a nonlinear fitting routine is the most direct, though, and gives excellent agreement in practice.[18]

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the Belgian Government (Grant No. IUAP-16), the Belgian National Science Foundation (Grant No. FKFO 9.0103.93), and the University of Leuven (Grant No. GOA95/1).

[1] *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic, Orlando, 1987), Vol. 1.

[2] M. Kauranen, T. Verbiest, J. W. Meijer, E. E. Havinga, M. N. Teerenstra, A. J. Schouten, R. J. M. Nolte, and A. Persoons, Adv. Mater. **7**, 641 (1995).

[3] *Selected Papers on Natural Optical Activity*, edited by A. Lakhtakia (SPIE, Bellingham, 1990).

[4] T. Petralli-Mallow, T. M. Wong, J. D. Byers, H. I. Yee, and J. M. Hicks, J. Phys. Chem. **97**, 1383 (1993).

[5] L. Hecht and L. D. Barron, Mol. Phys. **89**, 61 (1996).

[6] H. I. Yee, J. D. Byers, T. Petralli-Mallow, and J. M. Hicks, in *Laser Techniques for State-Selected and State-to-State Chemistry*, edited by C. Ng [Proc. SPIE **1858**, 343 (1993)].

[7] J. D. Byers, H. I. Yee, T. Petralli-Mallow, and J. M. Hicks, Phys. Rev. B **49**, 14 643 (1994).

[8] J. D. Byers and J. M. Hicks, Chem. Phys. Lett. **231**, 216 (1994).

[9] J. M. Hicks, T. Petralli-Mallow, and J. D. Byers, Faraday Discuss. **99**, 341 (1994).

[10] T. Verbiest, M. Kauranen, A. Persoons, M. Ikonen, J. Kurkela, and H. Lemmetyinen, J. Am. Chem. Soc. **116**, 9203 (1994).

[11] M. J. Crawford, S. Haslam, J. M. Probert, Y. A. Gruzdkov, and J.

G. Frey, Chem. Phys. Lett. **229**, 260 (1994).
[12] M. Kauranen, T. Verbiest, and A. Persoons, Nonlinear Opt. **8**, 243 (1994).
[13] J. J. Maki and A. Persoons, J. Chem. Phys. **104**, 9340 (1996).
[14] J. J. Maki, M. Kauranen, and A. Persoons, Phys. Rev. B **51**, 1425 (1995).
[15] R. Stolle, M. Loddoch, and G. Marowsky, Nonlinear Opt. **8**, 79 (1994).
[16] L. Hecht and L. D. Barron, Chem. Phys. Lett. **225**, 525 (1994); J. Mol. Struct. **348**, 217 (1995).
[17] T. Verbiest, M. Kauranen, J. J. Maki, M. N. Teerenstra, A. J. Schouten, R. J. M. Nolte, and A. Persoons, J. Chem. Phys. **103**, 8296 (1995).
[18] J. J. Maki, T. Verbiest, M. Kauranen, S. Van Elshocht, and A. Persoons, J. Chem. Phys. **105**, 767 (1996).
[19] J. D. Byers, H. I. Yee, and J. M. Hicks, J. Chem. Phys. **101**, 6233 (1994).
[20] H. I. Yee, J. D. Byers, and J. M. Hicks, Proc. SPIE **2125**, 119 (1994).
[21] T. Verbiest, M. Kauranen, Y. Van Rompaey, and A. Persoons, Phys. Rev. Lett. **77**, 1456 (1996).
[22] M. Kauranen, T. Verbiest, J. J. Maki, and A. Persoons, J. Chem. Phys. **101**, 8193 (1994).
[23] M. Kauranen, J. J. Maki, and A. Persoons, Proc. SPIE **2527**, 328 (1995).
[24] B. U. Felderhof, A. Bratz, G. Marowsky, O. Roders, and F. Sieverdes, J. Opt. Soc. Am. B **10**, 1824 (1993); **11**, 394(E) (1994).
[25] O. Roders, O. Befort, G. Marowsky, D. Möbius, and A. Bratz, Appl. Phys. B **59**, 537 (1994).
[26] F. Geiger, R. Stolle, G. Marowsky, M. Palenberg, and B. U. Felderhof, Appl. Phys. B **61**, 135 (1995).
[27] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1989), p. 488.
[28] J. E. Sipe, J. Opt. Soc. Am. B **4**, 481 (1987).
[29] E. Schwarzberg, G. Berkovic, and G. Marowsky, Appl. Phys. A **59**, 631 (1994).