Uniqueness of determination of second-order nonlinear optical expansion coefficients of thin films

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Second-harmonic generation from surfaces and thin films can be described by up to three nonlinear expansion coefficients, which are associated with the quadratic combinations of the *p*- and *s*-polarized components of the fundamental beam and specific to the measured signal. It has been shown that the relative complex values of the coefficients can be uniquely determined by using a quarter-wave-plate to continuously vary the state of polarization of the fundamental beam [J. J. Maki, M. Kauranen, T. Verbiest, and A. Persoons, Phys. Rev. B **55**, 5021 (1997)]. The proof is based on a specific and experimentally convenient initial state of polarization before the wave plate and on the assumption of the most general experimental situation where all three coefficients are nonvanishing, which implies that the sample or the experimental setup is chiral. We show both experimentally and theoretically that, surprisingly, the traditional experimental configuration fails in yielding unique values in a more specific, but common, achiral case. We identify new initial states of polarization that allow the coefficients to be uniquely determined even in the achiral case.

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I. INTRODUCTION

Techniques based on second-order nonlinear optical processes such as second-harmonic generation (SHG) are attractive tools to study interfaces, surfaces, and thin films.[1] This feature arises from the fact that, within the electric-dipole approximation, second-order processes are forbidden in bulk media with inversion symmetry. However, they are allowed at surfaces where the symmetry is necessarily broken.

The proper quantity to describe SHG is the susceptibility tensor, which is directly associated with the macroscopic structure of the material. Accurate determination of the susceptibility tensor components is important for both the characterization of new materials and fundamental studies of surface and interface effects. However, the tensor components are not accessible directly from experimental measurements. Instead, in a surface geometry (Fig. 1), the intensity of any SHG signal from the nonlinear surface layer can be expressed in the general form[2]

$$I^{SHG} = |fE_p^2 + gE_s^2 + hE_pE_s|^2, \tag{1}$$

where E_p and E_s are the *p*- and *s*-polarized (parallel and perpendicular to the plane of incidence, respectively) components of the beam at fundamental frequency, and the expansion coefficients f, g, and h are complex valued. The expansion coefficients are linear combinations of several components of the susceptibility tensor and also depend on the experimental geometry and the linear optical properties of the material. Equation (1) is completely general and applicable to surface-type samples of any symmetry as long as the changes in the polarizations of the fields due to linear properties of the sample can be neglected.[3] The equation also shows that the second-harmonic signal does not depend on the overall phase of the coefficients but only on their relative phases. Nevertheless, the expansion coefficients are the quantities which can be directly determined from experimental measurements.

The expansion coefficients can be determined by modulating the state of polarization of the fundamental beam.[2,4–11] Furthermore, it is commonly believed that the relative complex values of the coefficients can be uniquely determined by using a continuously rotating quarter-wave-plate for the polarization modulation.[5] This result has been proven for the most general case where all the three expansion coefficients are simultaneously present, i.e., when the sample[2,4,6–8] or the experimental setup[9–12] is chiral. In addition, the detailed proof of Ref. 5 is based on the assumption that the initial beam is *p* polarized before the quarter-wave-plate. This choice for the initial polarization is convenient in practice, because *p* polarization is easy to align in the laboratory. Because of the generality of the situation, one would expect the proof to hold for arbitrary samples, i.e., also for achiral situations. Achiral samples are still by far the most common cases encountered in surface and thin-film nonlinear optics.

In this paper, we show both experimentally and theoretically that the uniqueness proof of Ref. 5 is limited to chiral

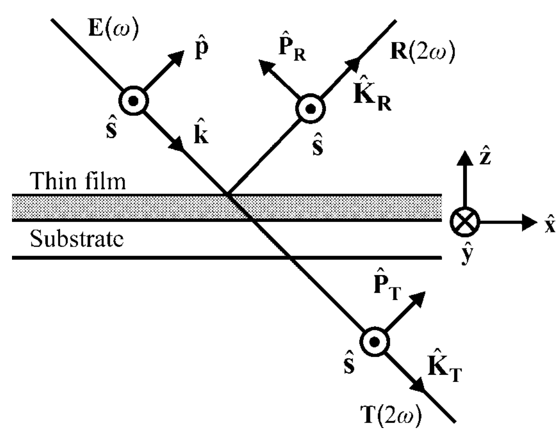

FIG. 1. Geometry of surface or thin-film second-harmonic generation. $\mathbf{E}(\omega)$ is the electric field vector of the fundamental beam incident on the sample, while $\mathbf{R}(2\omega)$ and $\mathbf{T}(2\omega)$ are the field vectors of the SHG beams in the reflected and transmitted directions, respectively. The fields are most naturally divided into *p* and *s* components (parallel and normal to the plane of incidence, respectively). The coordinate system *xyz* associated with the sample is also shown.

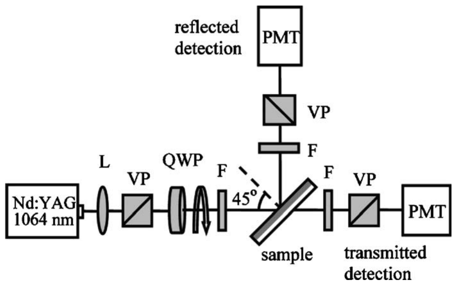

FIG. 2. Geometry for measuring the susceptibility tensor components by second-harmonic generation. QWP, zero-order quarter-wave-plate; L, 50 cm focal-length lens; VP, variable-angle polarizer; F, filter; and PMT, photomultiplier tube.

cases and is therefore not valid for achiral cases. We also show that the uniqueness can be recovered by properly choosing the initial polarization of the fundamental field before the quarter-wave-plate.

II. EXPERIMENTAL DETAILS AND MODEL DATA

An achiral sample is commonly encountered for the cases of thin organic films that consist of achiral molecules that are isotropically distributed in the plane of the sample ($C_{\infty v}$ symmetry). Furthermore, the experimental geometry is also achiral when p- or s-polarized SHG light, not their combination, is detected.[9–12] In such a case, where both the sample and setup are achiral, the p-polarized SHG signal is described by only the expansion coefficients f and g and the s-polarized signal by h, i.e., Ref. 10,

$$I_p^{SHG} = |fE_p^2 + gE_s^2|^2, \tag{2}$$

$$I_s^{SHG} = |hE_pE_s|^2. \tag{3}$$

It is evident that Eq. (3) provides no information about the relative values of the expansion coefficients. However, the intensity of the p-polarized second-harmonic signal described by Eq. (2) depends on the relative values of the expansion coefficients f and g.

Our experimental setup for surface second-harmonic generation is shown in Fig. 2. Infrared radiation from a Nd:YAG (yttrium aluminum garnet) laser (1064 nm, 0.15 mJ, 60 ps, 1000 Hz) is the source of fundamental light for second-harmonic generation. The beam is applied to the sample at an incident angle of 45°. A 50 cm focal-length lens is used to make the beam weakly focused to a spot size of approximately 0.5 mm at the sample to achieve sufficient separation of its reflections from the front and back surfaces of the glass substrate. The polarization state of the beam is first cleaned with a variable-angle calcite Glan polarizer (extinction ratio $\sim 4 \times 10^{-6}$) to define the polarization of the fundamental beam, such as p-, s-, and $p \pm s$-polarized light, and then modulated by rotating a zero-order quarter-wave-plate (QWP). We refer to the beam before (after) the QWP as the initial (incident) beam. A long wavelength pass filter before the sample blocks the SHG light generated by the preceding optical components. The SHG components of the transmitted and reflected beams are isolated with short wavelength pass filters and 532 nm interference filters and detected with a photomultiplier tubes (PMTs). Analyzers before the PMTs are used to detect the p-polarized component of the second-harmonic signal.

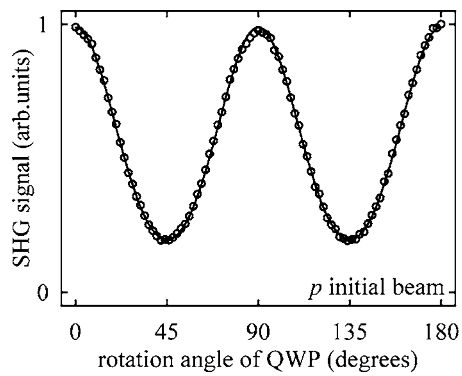

FIG. 3. Normalized p-polarized second-harmonic signal for p-polarized initial light. The circles are the original experimental data; the solid and dashed lines are the fit curves with different initial values of the fit coefficients. Note that the two fits cannot be resolved because they overlap.

In our experiments, we use Z-type Langmuir-Blodgett films of terthiophene-vinylbenzoate whose structure has been described earlier.[13] The films belong to the symmetry group $C_{\infty v}$. Our first measurements are performed using the traditional configuration where the initial fundamental beam before the quarter-wave-plate is p polarized. The result for the transmitted second-harmonic signal and its fits to Eq. (2) are shown in Fig. 3. In addition, the relative fitted values of the expansion coefficients f and g are shown in Table I.

The results shown in Fig. 3 and Table I indicate that the experimental results can be fitted equally well with two completely different sets of relative values of the fit coefficients. The expansion coefficients obtained from the measurements are therefore not unique. In addition, the disagreement is substantial, because the two sets of fit coefficients differ by more than one order of magnitude in value. The present results are therefore contradictory with the uniqueness proof of Ref. 5. However, the proof is based on the assumption that all three expansion coefficients f, g, and h are nonvanishing, whereas h vanishes for the present case. Therefore, the existing contradiction may arise from the subtle difference between the theory behind the proof and the present experi-

TABLE I. Fitted relative values of the expansion coefficients f and g for p-polarized second-harmonic detection from the measured experimental data obtained by using p-polarized initial light. The subscripts 1 and 2 denote the real and imaginary parts of the coefficients, respectively. The coefficient f is normalized to unity.

Initial values	Fitted values ($f=1$)
$g_1=0.1$	$g_1=0.1423$
$g_2=0.1$	$g_2=-0.0072$
$g_1=2$	$g_1=1.8577$
$g_2=0.1$	$g_2=-0.0072$

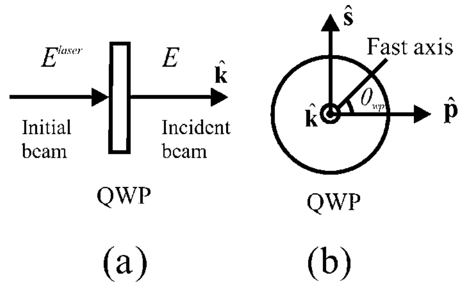

FIG. 4. (a) Preparation of the polarization state of the initial fundamental beam with a quarter-wave plate. (b) Definition of the rotation angle θ_{wp} of QWP with respect to $\hat{\mathbf{p}}$ and $\hat{\mathbf{s}}$ directions.

ment. We will next proceed to investigate whether this is the case.

III. THEORY

We take the fundamental laser beam as a plane wave but allow the possibility that its initial linear polarization before the quarter-wave-plate is arbitrary (Fig. 4). We therefore express the electric field amplitude of the laser beam in terms of its p- and s-polarized components as

$$E^{laser} = E_p^{laser}\hat{\mathbf{p}} + E_s^{laser}\hat{\mathbf{s}}, \tag{4}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{s}}$ are the polarization unit vectors. After passing through the quarter-wave-plate, the beam incident on the sample is of the form

$$E = E_p\hat{\mathbf{p}} + E_s\hat{\mathbf{s}}, \tag{5}$$

where the p and s components are

$$\begin{bmatrix} E_p \\ E_s \end{bmatrix} = T\begin{bmatrix} E_p^{laser} \\ E_s^{laser} \end{bmatrix}, \tag{6}$$

and the Jones matrix for a quarter-wave-plate[14] is

$$T = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 - i\cos 2\theta_{wp} & -i\sin 2\theta_{wp} \\ -i\sin 2\theta_{wp} & 1 + i\cos 2\theta_{wp} \end{bmatrix}, \tag{7}$$

where θ_{wp} is the rotation angle of the quarter-wave-plate measured as the angle between the fast axis of the quarter-wave-plate and the p direction.

Equation (1) shows that the second-harmonic signal does not depend on the overall phase of the parameters but only on the relative phase among them. Therefore, we take the expansion coefficients to be of completely general forms $f = f_1 e^{i\varphi}$ with $f_1 > 0$ and $g = (g_1 + ig_2)e^{i\varphi}$. These forms make the overall phase of the expansion coefficients explicit and the subscripts 1 and 2 denote the real and imaginary parts of coefficients, respectively. After using these forms of the expansion coefficients and Eqs. (5)–(7), we find from Eq. (2) that the intensity of the p-polarized SHG signal can always be expanded as a Fourier series of the angle θ_{wp} of the wave plate as[5]

$$I^{SHG} = a_0 + \sum_{m=1}^{4}[a_m\cos(2m\theta_{wp}) + b_m\sin(2m\theta_{wp})]. \tag{8}$$

Note that the Fourier coefficients are uniquely defined. Therefore, the uniqueness of the relative values of the expansion coefficients depends on whether they can be uniquely solved from the Fourier coefficients.[5]

We first consider the traditional case where the initial beam before the wave plate is p-polarized [$E_p^{laser}=1$ and $E_s^{laser}=0$ in Eq. (4)]. The nonvanishing Fourier coefficients are then found to be

$$a_0 = \frac{19}{32}f_1^2 + \frac{3}{32}(g_1^2 + g_2^2) - \frac{3}{16}f_1 g_1, \tag{9a}$$

$$a_1 = \frac{1}{4}f_1 g_2, \tag{9b}$$

$$a_2 = \frac{3}{8}f_1^2 - \frac{1}{8}(g_1^2 + g_2^2) + \frac{1}{4}f_1 g_1, \tag{9c}$$

$$a_3 = -\frac{1}{4}f_1 g_2, \tag{9d}$$

$$a_4 = \frac{1}{32}f_1^2 + \frac{1}{32}(g_1^2 + g_2^2) - \frac{1}{16}f_1 g_1. \tag{9e}$$

By solving Eqs. (9a)–(9e), the solutions for the expansion coefficients are found to be

$$f_1 = \pm\sqrt{2a_2 + 8a_4}, \tag{10}$$

$$g_1 = f_1 \pm \frac{2\sqrt{f_1^4 - 2a_2 f_1^2 - 4a_1^2}}{f_1}, \tag{11}$$

$$g_2 = \frac{4a_1}{f_1}. \tag{12}$$

It is obvious that only one solution for the expansion coefficient f_1 in Eq. (10) satisfies the requirement $f_1 > 0$. In spite of this requirement, it is clear that the real part of expansion coefficient g is not unique. This indicates that the use of a p-polarized initial beam does not give unique values of the expansion coefficients in the achiral case. This result explains the two equally good fits in our model data. Furthermore, it shows that the earlier result of Ref. 5 about the uniqueness is limited to chiral cases.

However, unique determination of the expansion coefficients is very important to obtain reliable values of the components of susceptibility tensor for a nonlinear optical material. We next proceed to investigate whether the coefficients can be determined uniquely using different choices of the initial polarization. We will consider the most obvious cases of s-, $p+s$-, and $p-s$ initial polarizations.

When the initial beam is s polarized, the Fourier coefficients are found to be

$$a_0 = \frac{3}{32}f_1^2 + \frac{19}{32}(g_1^2 + g_2^2) - \frac{3}{16}f_1 g_1, \tag{13a}$$

$$a_1 = \frac{1}{4}f_1 g_2, \tag{13b}$$

$$a_2 = -\frac{1}{8}f_1^2 + \frac{3}{8}(g_1^2 + g_2^2) + \frac{1}{4}f_1 g_1, \tag{13c}$$

$$a_3 = -\frac{1}{4}f_1 g_2, \tag{13d}$$

$$a_4 = \frac{1}{32}f_1^2 + \frac{1}{32}(g_1^2 + g_2^2) - \frac{1}{16}f_1 g_1. \tag{13e}$$

By combining and solving Eqs. (13a)–(13e), we first obtain four solutions for f_1,

$$f_1 = \pm\sqrt{2a_2 + 40a_4 \pm 8\sqrt{4a_2 a_4 + 16a_4^2 - a_1^2}}. \tag{14}$$

Under the requirement that $f_1 > 0$, we find the final solution for the expansion coefficients as

$$f_1 = \sqrt{2a_2 + 40a_4 \pm 8\sqrt{4a_2 a_4 + 16a_4^2 - a_1^2}}, \tag{15}$$

$$g_1 = \frac{2a_2 - 24a_4 + f_1^2}{2f_1}, \tag{16}$$

$$g_2 = \frac{4a_1}{f_1}. \tag{17}$$

As a consequence, the expansion coefficients are still not uniquely determined when the initial beam is s polarized.

When the initial fundamental beam is taken to be $(p+s)$-polarized light [$E_p^{laser} = E_s^{laser} = \frac{1}{\sqrt{2}}$ in Eq. (4)], the Fourier coefficients are

$$a_0 = \frac{9}{32}(f_1^2 + g_1^2 + g_2^2) - \frac{1}{16}f_1 g_1, \tag{18a}$$

$$a_1 = -\frac{1}{4}f_1 g_2, \tag{18b}$$

$$a_2 = -\frac{1}{2}f_1 g_1, \tag{18c}$$

$$a_3 = \frac{1}{4}f_1 g_2, \tag{18d}$$

$$a_4 = -\frac{1}{32}(f_1^2 + g_1^2 + g_2^2) + \frac{1}{16}f_1 g_1, \tag{18e}$$

$$b_2 = \frac{1}{4}(f_1^2 - g_1^2 - g_2^2). \tag{18f}$$

From these equations, the solution for the coefficient f_1 is first found to be

$$f_1 = \pm\sqrt{2b_2 \pm 2\sqrt{b_2^2 + a_2^2 + 4a_3^2}}. \tag{19}$$

It is evident that the only solution that fulfills the requirement $f_1 > 0$ is then

$$f_1 = \sqrt{2b_2 + 2\sqrt{b_2^2 + a_2^2 + 4a_3^2}}, \tag{20}$$

$$g_1 = -\frac{2a_2}{f_1}, \tag{21}$$

$$g_2 = \frac{4a_3}{f_1}. \tag{22}$$

The results indicate that the real and imaginary parts of the expansion coefficient g can also be uniquely determined under the use of a combination of p- and s-polarized light as initial light.

When the initial light is $(p-s)$ polarized (i.e., $E_p^{laser} = \frac{1}{\sqrt{2}}$ and $E_s^{laser} = -\frac{1}{\sqrt{2}}$), we find the Fourier coefficients

$$a_0 = \frac{9}{32}(f_1^2 + g_1^2 + g_2^2) - \frac{1}{16}f_1 g_1, \tag{23a}$$

$$a_1 = -\frac{1}{4}f_1 g_2, \tag{23b}$$

$$a_2 = -\frac{1}{2}f_1 g_1, \tag{23c}$$

$$a_3 = \frac{1}{4}f_1 g_2, \tag{23d}$$

$$a_4 = -\frac{1}{32}(f_1^2 + g_1^2 + g_2^2) + \frac{1}{16}f_1 g_1, \tag{23e}$$

$$b_2 = \frac{1}{4}(-f_1^2 + g_1^2 + g_2^2). \tag{23f}$$

The solution for the expansion coefficient f_1 is now

$$f_1 = \pm\sqrt{-2b_2 \pm 2\sqrt{b_2^2 + a_2^2 + 4a_3^2}}, \tag{24}$$

and final solutions that fulfill the requirement $f_1 > 0$ are

$$f_1 = \sqrt{-2b_2 + 2\sqrt{b_2^2 + a_2^2 + 4a_3^2}}, \tag{25}$$

$$g_1 = -\frac{2a_2}{f_1}, \tag{26}$$

$$g_2 = \frac{4a_3}{f_1}. \tag{27}$$

The above results can be summarized by the requirement that it is necessary to use a combination of p- and s-polarized initial light before the quarter-wave-plate in order to obtain unique relative values of the expansion coefficients f and g when the sample and setup are achiral.

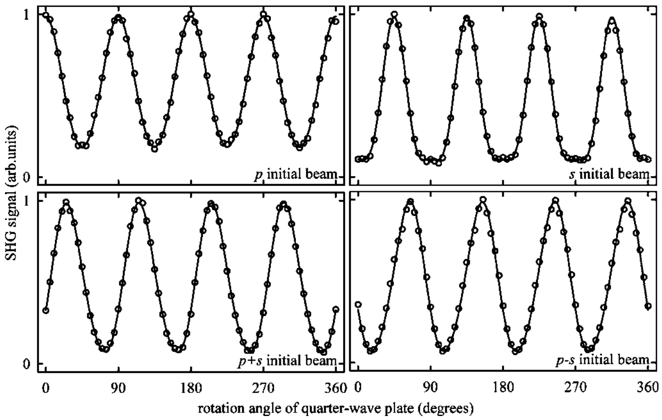

FIG. 5. Normalized p-polarized second-harmonic signals for p-, s-, $p+s$-, and $p-s$-polarized initial lights. The circles are the original experimental data; the solid and dashed lines are fit curves with different initial values of the fit coefficients.

TABLE II. Fitted relative values of the expansion coefficients f and g for p-polarized second-harmonic detection under the use of p-, s-, $(p+s)$-, and $(p-s)$-polarized light as an initial beam. The coefficient f is normalized to unity. The correct and mutually agreeing values are indicated by boldface. Note that the imaginary parts are essentially vanishing as expected for the present sample.

Polarization of initial beam	Initial values	Fitted values ($f=1$)
p	$g_1=0.1$ $g_2=0.1$	$g_1=$**0.1358** $g_2=0.0042$
	$g_1=2$ $g_2=0.1$	$g_1=1.8642$ $g_2=0.0042$
s	$g_1=0.1$ $g_2=0.1$	$g_1=-0.1976$ $g_2=0.0107$
	$g_1=2$ $g_2=0.1$	$g_1=$**0.1417** $g_2=0.0055$
$p+s$	Arbitrary	$g_1=$**0.1460** $g_2=0.0052$
$p-s$	Arbitrary	$g_1=$**0.1412** $g_2=0.0039$

IV. EXPERIMENTAL VERIFICATION

To test the validity of the theory, we use a variable-angle polarizer before the quarter-wave-plate to obtain different initial polarizations. The results for p, s, $p+s$, and $p-s$ initial polarizations are shown in Fig. 5, respectively. In addition, the fitted values of the expansion coefficients f and g are shown in Table II.

Table II indicates that the fitted values agree well with the theoretical analysis for all the four different cases of the initial polarization. In particular, the p and s initial polarizations lead to two equally good fits, i.e., the coefficients cannot be determined uniquely. The $p+s$ and $p-s$ initial polarizations, on the other hand, lead to unique expansion coefficients. We found that the fitted values of the expansion coefficients for p- and s-polarized initial beams are dependent on the initial values, while they are independent of the initial values for the case of a combination of p and s polarization initial beam. Furthermore, the unique and correct values obtained from all the four measurements are close to each other. This also suggests that a more reliable solution could be obtained by combining results for a number of different choices of the initial polarization.

V. CONCLUSION

We have considered the uniqueness of the determination of the second-order nonlinear optical expansion coefficients of surfaces and thin films by a technique based on continuous modulation of the state of polarization of the fundamental beam by a quarter-wave-plate. We have shown that the commonly used technique where the initial polarization before the quarter-wave-plate is p does not lead to unique values of the expansion coefficients for achiral cases, i.e., when only f and g coefficients are present. The earlier proof of the uniqueness is therefore limited to chiral cases where all the three coefficients f, g, and h contribute. To overcome this problem, we have extended the study to other choices of the initial polarization. The result is that the relative values of expansion coefficients f and g for achiral cases can be uniquely determined when the initial beam consists of a superposition between the p- and s-polarized components, the most natural choices being $p\pm s$ polarizations.

The theoretical predictions were verified in an experiment using an achiral and isotropic thin film of nonlinear molecules deposited on a substrate. Furthermore, they suggest that the reliability of the values of the expansion coefficients could be further improved by combining results from measurements where different initial polarizations were used. The possibility of obtaining unique values of the expansion coefficient is a prerequisite for any subsequent determination of the components of the nonlinear susceptibility tensor.

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