Advantages of polarized two-beam second-harmonic generation in precise characterization of thin films

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Polarized second-harmonic generation using two fundamental beams, instead of one, offers significant advantages for characterizing nonlinear optical thin films. The technique is more precise and allows the internal consistency of the results to be verified. The superiority of the two-beam arrangement over the traditional single-beam arrangement is demonstrated by determining the susceptibility tensors of Langmuir–Blodgett films. We show that, for a well-understood reference sample, the results obtained using two fundamental beams agree qualitatively with those obtained with a single fundamental beam, but are more precise. In a more complicated situation, however, the single-beam technique appears to work well but yields results that are, in fact, incorrect. The two-beam technique, instead, yields clearly inconsistent results, thereby highlighting systematic errors in the experimental arrangement or in the theoretical model used to interpret the results. [DOI: 10.1063/1.1710858]

I. INTRODUCTION

Second-order nonlinear optical processes, such as second-harmonic generation (SHG) and sum-frequency generation (SFG), are dipole forbidden in bulk media with inversion symmetry but allowed wherever the symmetry is broken.[1] SHG and SFG are therefore attractive methods to study surfaces, interfaces, and thin films.[2,3] The key quantity describing the processes is the second-order susceptibility tensor, which is directly associated with the macroscopic structure of the sample. The accurate determination of the tensor is of great importance both for the characterization of new materials and for fundamental studies of surface and interface effects.

Unfortunately, the susceptibility tensor is not directly accessible in an experiment. Its determination occurs in two distinct parts: the first requires a precise experimental characterization of the nonlinear response of the sample, while the second consists of extracting the susceptibility tensor from experimental data using a theoretical model. The results for the susceptibility depend strongly on the quality of the experimental data and on the details of the theoretical model used.[4] Both aspects should therefore be thoroughly investigated.

Both SHG and SFG provide intrinsic surface sensitivity on the scale of atomic monolayers and have found widespread applications in surface studies.[2–5] However, the main focus for the two methods has historically been different. SFG has mostly been used to obtain spectroscopic information on the electronic and vibrational states of the system.[6] On the other hand, studies aiming at a precise determination of the susceptibility tensor (e.g., for studies of molecular orientation) have generally been performed using SHG.[7–10]

SFG experiments involve two separate light sources and, therefore, are naturally conducted using a geometry in which the two input beams are directed onto the sample at different angles. Such noncollinear arrangement allows for spatial separation of the signal from the input beams, thereby eliminating the need for spectral filtering. The directional properties of noncollinear arrangements can be exploited in SHG experiments as well. Muenchausen *et al.* demonstrated that the noise due to broadband fluorescence and scattered light is effectively reduced in a noncollinear SHG geometry by spatially filtering the signal.[11] In spite of these advantages, SHG experiments are usually performed, for the sake of simplicity, using a single beam at the fundamental frequency.

Over the years, different SHG techniques have been proposed to determine the nonlinear susceptibility tensor.[2,3] Practically all measurements have been conducted using a single fundamental beam. Notable exceptions are Refs. 12 and 13, where a noncollinear SHG geometry with linearly polarized fundamental beams was used to determine the ratio of real-valued susceptibility components. In general, techniques that use only linearly polarized fundamental beams do not posses phase sensitivity and are therefore not suitable for the determination of complex-valued susceptibilities. Phase sensitivity can be achieved by introducing a circular component in the polarization state of the fundamental beam.[14] More advanced techniques involve continuous measurements of the SHG signal as a function of the fundamental polarization.[10] Such techniques allow the determination of

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the susceptibility tensor components without any prior assumptions but still have two important limitations that arise from the fact that a single fundamental beam is used. The measured polarization line shapes are sometimes complicated, which can prevent a precise characterization of the nonlinear optical response. Even more importantly, the techniques do not offer a direct way of verifying the quality of the experimental data or of the calculated susceptibility tensors. Such consistency tests are desirable, as they can be used to highlight possible systematic errors in the experimental setup or in the theoretical model used to interpret the results.

In this paper, we demonstrate the advantages of polarized SHG using two fundamental beams in the characterization of thin films as compared to the traditional single-beam arrangement. The technique allows the relative values of complex experimental parameters to be determined with increased precision. In addition, it provides direct ways to verify the internal consistency of the experimental data as well as that of the calculated susceptibility components. We measure the susceptibility components of Langmuir–Blodgett (LB) films of various thicknesses using both one- and two-beam polarized SHG arrangements. We show that, for relatively thick films, for which the contribution of the glass substrate to the nonlinear response is negligible, the results of the two-beam measurement agree qualitatively with those of the single-beam measurement, but are more precise. For thinner LB films where the substrate contribution is relatively more important, however, the results of the two techniques are completely different. While the single-beam arrangement appears to work but in fact yields incorrect results, the two-beam technique yields internally inconsistent results, thereby highlighting systematic errors in the procedure.

The structure of the paper is as follows: In Sec. II, we present the main concepts of both single- and two-beam polarized SHG techniques for the characterization of the nonlinear optical response of thin films. The theoretical framework of the techniques is first illustrated for samples of arbitrary symmetry, and then for the common case of achiral samples with in-plane isotropy. Section III outlines the extraction of the susceptibility tensor from experimental data. The experimental measurements on LB films and their results are described in detail in Secs. IV and V, respectively. Concluding remarks are given in Sec. VI.

II. CHARACTERIZATION OF THE NONLINEAR OPTICAL RESPONSE

A. Single-beam arrangement, general symmetry

We consider a situation where a laser beam at the fundamental frequency ω and with field amplitude $\mathbf{A}(\omega)$ is incident on a thin film of arbitrary symmetry and transmitted or reflected second-harmonic light is detected (Fig. 1). For sufficiently thin films, polarization effects due to linear light propagation in the film can be neglected. For weakly focused beams, the fields are most naturally divided into p and s components (parallel and normal to the plane of incidence, respectively). Regardless of sample symmetry, a given second-harmonic signal is proportional to the nonlinear polarization and must therefore be of the form

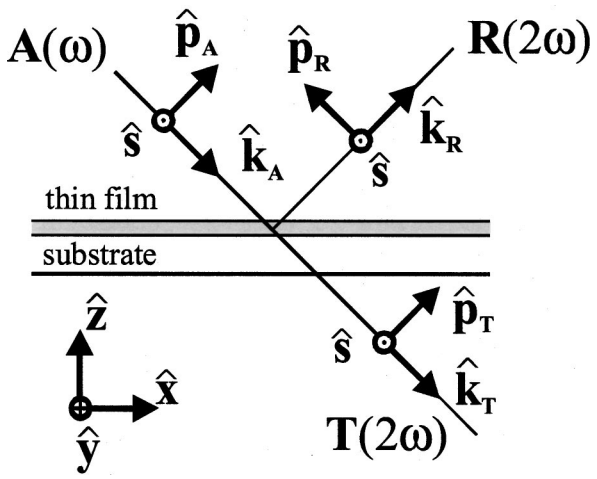

FIG. 1. Geometry of the single-beam experiment to determine the susceptibility tensor components of a thin-film sample. $\mathbf{A}(\omega)$ is the field vector of the fundamental beam incident on the sample, while $\mathbf{R}(2\omega)$ and $\mathbf{T}(2\omega)$ are the field vectors of the SHG beams in, respectively, reflected and transmission directions. The fields are most naturally divided into p and s components (parallel and normal to the plane of incidence, respectively). During the experiment, the polarization of the incoming beam is continuously modulated. The coordinate system x, y, z, associated with the sample is also shown.

$$I_j(2\omega)=|f_jA_p^2(\omega)+g_jA_s^2(\omega)+h_jA_p(\omega)A_s(\omega)|^2, \qquad (1)$$

where the subscript j denotes the polarization of the second-harmonic signal.

The expansion coefficients f_j, g_j, and h_j in Eq. (1) are linear combinations of the susceptibility components and depend on the linear optical properties of the sample.[15] The coefficients are, in general, complex quantities and can be interpreted as effective susceptibility components in the p and s reference system. However, the coefficients are not pure material constants, as they also depend on the experimental geometry.[15] Nevertheless, f_j, g_j, and h_j are the quantities that can be measured most directly in an experiment. Since they represent the starting point for any successive calculation, special attention should be given to their precise determination.

The coefficients are most conveniently determined by recording a particular SHG signal while the polarization of the incoming beam is continuously modulated.[14] The recorded polarization pattern can then be fitted with the model of Eq. (1) to determine f_j, g_j, and h_j. As the measurements are insensitive to absolute phase, one of the expansion coefficients can always be taken as real. Nevertheless, the pattern depends simultaneously on no less than five real fitting parameters and is therefore sometimes not very sensitive to small changes in their values. This fact may compromise the precise determination of the expansion coefficients.

The full characterization of the nonlinear response of the sample for a given experimental geometry requires two distinct sets of expansion coefficients f_j, g_j, and h_j, for two orthogonal polarization components (e.g., p and s) of the

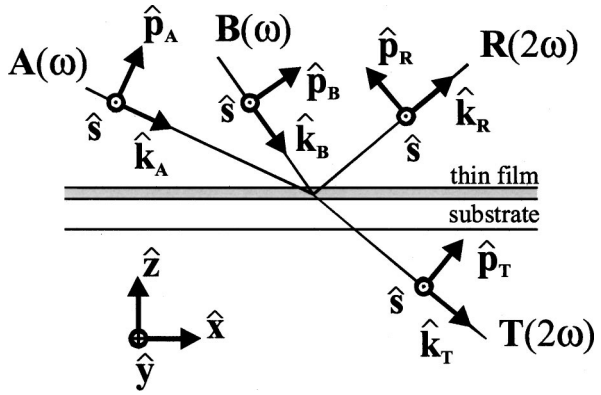

FIG. 2. Geometry to measure the susceptibility components by two-beam SHG. The SHG light produced jointly by both fundamental beams is detected in the transmitted or reflected directions. The polarization of the control beam $\mathbf{A}(\omega)$ is kept fixed during the measurement, while the polarization of the probe beam $\mathbf{B}(\omega)$ is continuously modulated. The coordinate system *x*, *y*, *z*, associated with the sample is also shown.

SHG signal. The relative complex values of the coefficients belonging to a given set (*p* or *s*) can be determined separately by detecting *p*- and *s*-polarized SHG signals, respectively. Absolute calibration of the SHG signals allows relating the absolute magnitudes of the coefficients belonging to different sets. However, besides being impractical and subject to errors, this procedure does not allow determining phase differences between *p*- and *s*-polarized coefficients. An alternative approach consists of introducing complex scaling factors unique to each measurement.[10] A drawback of this approach is that it increases the number of unknowns in the problem, as the complex scaling factors must be determined together with the susceptibility components.

A more practical approach to determine phase differences between *p*- and *s*-polarized coefficients and to avoid the need to calibrate absolute signal levels, is to mix the *p*- and *s*-polarized SHG signals in detection. For example, the SHG signal detected through an analyzer placed at $\pm 45°$ with respect to the plane of incidence is of the form

$$I_{\pm 45}(2\omega) = |(f_p \pm f_s)A_p^2(\omega) + (g_p \pm g_s)A_s^2(\omega) + (h_p \pm h_s)A_p(\omega)A_s(\omega)|^2. \quad (2)$$

As is evident from Eq. (2), mixing introduces interference between *p*- and *s*-polarized coefficients. Measurements at both $+45°$ and $-45°$ are needed in order to resolve the individual coefficients. This procedure yields the minimum amount of experimental information needed to calculate all six expansion coefficients f_j, g_j, and h_j $(j=s,p)$. However, it does not offer a natural way to verify the quality of the experimental data.

B. Two-beam arrangement, general symmetry

To overcome the problems of the single-beam setup, we use an arrangement in which two beams at the fundamental frequency are mixed in the nonlinear sample to produce reflected or transmitted second-harmonic light (Fig. 2).[4]

TABLE I. Convenient combinations of the control and signal polarizations of the two-beam setup and the expansion coefficients determined for a sample of arbitrary symmetry.

Measurement	Control	Signal	α_j	β_j
1	$\pm 45°$	*p*	$f_p \pm k_p$	$h_p \pm g_p$
2	$\pm 45°$	*s*	$f_s \pm k_s$	$h_s \pm g_s$
3	*p*	$\pm 45°$	$f_p \pm f_s$	$h_p \pm h_s$
4	*s*	$\pm 45°$	$k_p \pm k_s$	$g_p \pm g_s$
5	*p*	*p*	f_p	h_p
6	*p*	*s*	f_s	h_s
7	*s*	*p*	k_p	g_p
8	*s*	*s*	k_s	g_s

For a sample of arbitrary symmetry, a given SHG signal produced jointly by the two fundamental beams (*A* and *B*) can be expressed as

$$I_j(2\omega) = |f_j A_p(\omega)B_p(\omega) + g_j A_s(\omega)B_s(\omega) + h_j A_p(\omega)B_s(\omega) + k_j A_s(\omega)B_p(\omega)|^2. \quad (3)$$

As the terms $A_p(\omega)B_s(\omega)$ and $A_s(\omega)B_p(\omega)$ are distinct, contrariwise to the case where a single fundamental beam is used, four expansion coefficients f_j, g_j, h_j, and k_j are now needed to completely specify a given SHG signal. This may at first appear as an additional complication compared to the single-beam arrangement. However, once the polarization of one fundamental beam (control beam, e.g., beam *A*) is fixed, Eq. (3) implies that any SHG signal is completely specified by only two parameters,

$$I_j(2\omega) = |\alpha_j B_p(\omega) + \beta_j B_s(\omega)|^2. \quad (4)$$

The parameters α_j and β_j are determined by recording the SHG signal while the polarization of the fundamental beam *B* (probe beam) is continuously modulated. Assuming one parameter to be real, the recorded pattern depends on only three real parameters. Such simple dependence allows a very precise determination of the experimental parameters α_j and β_j.

Similarly to the single-beam setup, the full characterization of the SHG response for a given experimental geometry requires two distinct sets of expansion coefficients f_j, g_j, h_j, and k_j, with $j=p$, *s*. Detecting *p*- or *s*-polarized SHG signals allows determining the relative values of the coefficients belonging to a given set. Interference between *p*- and *s*-polarized coefficients is induced by mixing the *p*- and *s*-polarized SHG signals in detection, in which case it is convenient to use either *p* or *s* control polarization.

The convenient combinations of control and signal polarizations are summarized in Table I. As in the single-beam case, measurements at both $+45°$ and $-45°$ polarizations are needed in order to resolve the individual coefficients. In fact, only four of the eight measurement types listed in Table I are sufficient to determine all eight expansion coefficients. For example, combining measurements of type 1, 3, and 5 allows determining the coefficients f_p, g_p, h_p, k_p, f_s, and h_s. Measurements of type 2 can then be used to calculate the missing coefficients g_s and k_s. The coefficients g_s and k_s can be calculated in a fully independent way if measurements of type 4 (instead of 2) are used. The reason for this additional

degree of freedom is the fact that, when measuring a signal at $\pm 45°$, the choice of either *p*- or *s*-polarized control beams offers two independent ways of generating interference between *p*- and *s*-polarized coefficients. This feature is an important advantage of the two-beam setup over the single beam setup and it can be used as a rigorous test of the internal consistency of the determined expansion coefficients and, consequently, as a measure of possible systematic errors in the experimental setup (such as misalignments or bad optical components).

C. Single-beam arrangement, $C_{\infty v}$ symmetry

Achiral thin films with in-plane isotropy belong to symmetry group $C_{\infty v}$, which includes many technologically relevant samples used in nonlinear optics. Since the experimental demonstration of our technique was performed on samples of symmetry $C_{\infty v}$, we briefly illustrate how the equations are modified for this particular case.

For samples of $C_{\infty v}$ symmetry, the susceptibility tensor $\chi^{(2)}_{ijk}$ has only three independent components $zxx=zyy$, $xxz=yyz$ and zzz, where x and y are the in-plane coordinates and z is the sample normal (Fig. 1). For the one-beam setup, it can then be shown that the coefficients h_p, f_s, and g_s vanish.[15] The *p*- and *s*-polarized second-harmonic signals are therefore described by

$$I_p(2\omega)=|f_p A_p^2(\omega)+g_p A_s^2(\omega)|^2, \tag{5}$$

$$I_s(2\omega)=|h_s|^2|A_p(\omega)A_s(\omega)|^2. \tag{6}$$

At first, the reduction of expansion coefficients seems to solve the problem of the complicated dependence of the SHG signal on the coefficients. The detection of *p*-polarized SHG signal allows namely a precise determination of the relative complex values of f_p and g_p. However, the *s*-polarized signal alone does not contain any information, since the interference between coefficients is completely lost and h_s appears only as an absolute scaling constant. The determination of the relative value of h_s with respect to f_p and g_p requires mixing the *p* and *s* polarization components of the SHG signal in detection. With an analyzer placed at $\pm 45°$ with respect to the plane of incidence, the detected SHG signal is of the form

$$I_{\pm 45}(2\omega)=|f_p A_p^2(\omega)+g_p A_s^2(\omega)\pm h_s A_p(\omega)A_s(\omega)|^2. \tag{7}$$

A single measurement (at $+45°$ or $-45°$) is then sufficient to determine all three expansion coefficients h_s, f_p, and g_p. Unfortunately, this procedure results again in signals depending simultaneously on five real parameters, similarly to the case of arbitrary symmetry [Eq. (1)], which may prevent a precise determination of the coefficients. In principle, one could use the values for f_p and g_p determined from the *p*-polarized measurement when fitting the line shape at $\pm 45°$. However, such multistep procedures result in increased experimental errors.

Also the second important limitation of the single-beam arrangement, the lack of a natural way to verify the quality of the experimental data, is still present when samples of symmetry $C_{\infty v}$ are investigated. It would be desirable to have at least two independent ways of determining a given expansion coefficient in order to address the proper operation of the experimental setup and to verify the assumption of $C_{\infty v}$ symmetry. Unfortunately, the single-beam setup offers only one way of determining the h_s coefficient. Measurements with the analyzer oriented at $+45°$ and $-45°$ only result in a change of the relative sign of h_s in Eq. (7) but cannot be considered as fully independent measurements.

TABLE II. Convenient combinations of the control and signal polarizations of the two-beam setup and the expansion coefficients determined for a sample of $C_{\infty v}$ symmetry.

Measurement	Control	Signal	α_j	β_j
1	$\pm 45°$	*p*	f_p	$\pm g_p$
2	$\pm 45°$	*s*	$\pm k_s$	h_s
3	*p*	$\pm 45°$	f_p	$\pm h_s$
4	*s*	$\pm 45°$	$\pm k_s$	g_p

D. Two-beam arrangement, $C_{\infty v}$ symmetry

For the two-beam arrangement and symmetry group $C_{\infty v}$, the coefficients h_p, k_p, f_s, and g_s vanish.[16] The *p* and *s* components of the second-harmonic signal are in this case given by

$$I_p(2\omega)=|f_p A_p(\omega)B_p(\omega)+g_p A_s(\omega)B_s(\omega)|^2, \tag{8}$$

$$I_s(2\omega)=|h_s A_p(\omega)B_s(\omega)+k_s A_s(\omega)B_p(\omega)|^2. \tag{9}$$

As for a general symmetry, once the polarization of the control beam is fixed, a given SHG signal is specified by only two parameters α_j and β_j [Eq. (4)], which can be determined very precisely.

The four expansion coefficients f_p, g_p, h_s, and k_s are determined by using the same polarization combinations described in Table II. Measuring a signal at $+45°$ or $-45°$ changes the relative sign of the respective coefficients α_j and β_j, but does not yield new information. Therefore, three measurements are sufficient to determine all four expansion coefficients. Combining measurements of type 1 and type 3 allows determining the expansion coefficients f_p, g_p, and h_s. A measurement of type 2 can then be used to calculate the missing coefficients k_s. The coefficient k_s can be determined in a fully independent way using a measurement of type 4 (instead of 2). Comparison of the two independent values of k_s is an excellent measure of the quality of experimental data. Inconsistency at this stage indicates a systematic error in the experimental system or a sample with symmetry lower than $C_{\infty v}$.

III. CALCULATION OF THE SUSCEPTIBILITY TENSOR

To extract the components of the susceptibility tensor, the experimentally determined coefficients must be compared to their expressions calculated using a theoretical model. The choice of the theoretical model is very important, since its details have strong influence on the results for the susceptibility components.[4]

When modeling the second-harmonic response of a thin film, the sample can be considered as a multilayer structure

(air–film–substrate–air). In our calculations, we use a model based on a Green's function formalism to calculate the fundamental fields inside the thin film and the actual second-harmonic field that exits the sample.[17] The model fully accounts for the linear properties of each layer and includes refraction, multiple reflections, and propagation effects over the thickness of the film, at both the fundamental and second-harmonic frequencies.

As mentioned above, two distinct sets of expansion coefficients for two orthogonal polarization components (e.g., *p* and *s*) of the SHG signal completely specify the nonlinear response of the sample for a given experimental geometry. However, for low symmetry samples, the number of unknowns (the independent susceptibility components) may be higher than the number of expansion coefficients available in a given geometry. For such samples, measurements must be performed in different geometries, e.g., by measuring in both reflection and transmission[10] and/or (for samples with in-plane anisotropy) rotating the sample about its surface normal.[18]

For samples of $C_{\infty v}$ symmetry, the problem has only three unknowns (the three independent susceptibility components zxx, xxz, and zzz). In the single-beam arrangement, the number of unknowns matches the number of independent experimental coefficients f_p, g_p, and h_s and a solution can always be found. For simple molecules (e.g., rodlike molecules with only one nonvanishing component of the molecular hyperpolarizability tensor) the results can, to some extent, be compared to the values predicted by the theory.[1] However, for more complicated molecules the three independent tensor components can assume arbitrary complex values. In such cases, there is no direct way of verifying whether the results obtained with the single-beam arrangement are correct.

In the two-beam arrangement, on the other hand, four expansion coefficients f_p, g_p, h_s, and k_s are accessible. The coefficients h_s and k_s both depend solely on the same tensor component xxz. Therefore, when solving for the susceptibility components, one of these coefficients can be neglected. Comparing the solutions obtained by neglecting, respectively, h_s and k_s allows verifying the consistency of the results. In particular, systematic errors in the experimental setup or in the theoretical model can be detected, even if the overall SHG response of the sample shows $C_{\infty v}$ symmetry.

IV. EXPERIMENTAL DETAILS

To demonstrate the advantages of the two-beam arrangement, we used LB films of terthiophene–vinylbenzoate (TSe, Fig. 3).[19] TSe is an asymmetric molecule with a conjugated π-electron bridge, and is therefore expected to have a second-order response. However, the molecule is far from being optimized for nonlinear optical applications (it does not include strong electron donors or acceptors) and therefore its response is expected to be low compared to widely used chromophores such as Disperse Red 1.

When embedded in an octadecyl amine (ODA) inactive matrix, TSe was found to form ordered head-to-tail (*Z*-type) LB films up to at least 100 molecular layers. The films have no preferred directions in the plane and therefore belong to the symmetry group $C_{\infty v}$. As mentioned above, for such symmetry group the expansion coefficients h_p, k_p, f_s, and g_s in Eqs. (1) and (3) vanish, where the subscripts refer to the polarization of the second-harmonic beam. The samples were investigated by linear absorption and ellipsometry to determine the complex refractive indices of the glass substrate (1.441 and 1.487) and of the LB films ($1.530+0.008i$ and $1.596+0.068i$) at both the fundamental and SHG frequencies (1064 nm and 532 nm wavelengths), respectively. The ellipsometric measurements also yielded a thickness of approximately 25 Å per TSe/ODA monolayer.

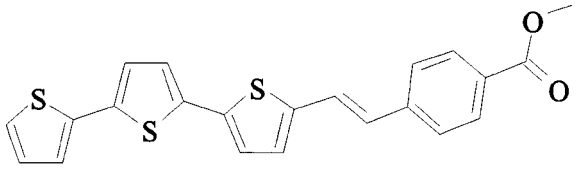

FIG. 3. Structure of terthiophene–vinylbenzoate (TSe). The molecular hyperpolarizability tensor of TSe is dominated by a single component along the charge transfer axis. When embedded in an octadecyl amine inactive matrix, TSe forms ordered head-to-tail (*Z*-type) LB films up to at least 100 molecular layers.

The molecular hyperpolarizability tensor of TSe is dominated by a single component along the charge transfer axis. For such rodlike molecules, the components ijk of the macroscopic susceptibility tensor are expected to be

$$zxx = xxz = zzz/r, \tag{10}$$

with r a real constant.[1] We note that the relation $zxx=xxz$ is *formally* similar to Kleinmann's symmetry, which is only valid under completely nonresonant conditions. However, for rodlike molecules the relation is a fundamental symmetry property of the susceptibility tensor and therefore remains valid in all spectral ranges.

Infrared radiation from a Q-switched Nd:YAG laser (1064 nm, ~5 mJ, 10 ns, 30 Hz) was used as the source of fundamental light for second-harmonic generation. For single-beam SHG measurements, the fundamental beam was applied to the sample at an incident angle of 45°. The beam was 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 fundamental beam was cleaned with a calcite Glan polarizer (extinction ratio $\sim 4\times 10^{-6}$) and then modulated by rotating a zero-order quarter-wave plate. A long pass filter before the sample blocked the SHG light generated by the preceding optical components. The SHG component of the transmitted beam was isolated with a short pass filter and a 532 nm interference filter and collected with a photomultiplier tube. To determine the expansion coefficients f_p, g_p, and h_s, the *p* and *s* polarization components of the SHG signal were mixed in detection with an analyzer placed at $\pm 45°$.

For two-beam SHG measurements, the fundamental beam was split into two beams of nearly the same intensity (control and probe), which were applied to the same spot of the film at incident angles of 40.9° and 51.7°, respectively. The control beam was linearly polarized by a calcite polar-

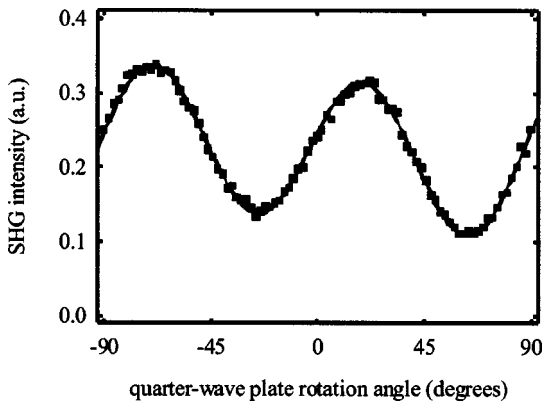

FIG. 4. A typical second-harmonic polarization line shape (squares) measured with the two-beam setup. During the measurement, the polarization of the fundamental beam is varied by a rotating quarter-wave plate. In this particular measurement, control and signal polarizations were, respectively, *s* and +45°. The fit (line) yields the complex relative value of the expansion coefficients k_s and g_p.

izer and its polarization state was kept fixed during each measurement. A given polarization component of the second-harmonic signal was then recorded while continuously varying the probe polarization using a quarter-wave plate. Each recorded polarization line shape could be described by only two expansion coefficients. All nonvanishing expansion coefficients f_p, g_p, h_s, and k_s were precisely determined using the polarization combinations listed in Table II. A typical polarization line shape and its corresponding fit are shown in Fig. 4. Since the measured SHG signal and the fundamental beams are spatially separated, no spectral filters were needed.

Our measurements were performed in transmission using substrates with parallel surfaces. In this geometry, the SHG signals include contributions also from both surfaces of the substrate and a dipole-forbidden contribution from the bulk of the substrate.[20] While the contribution of the clean surface of the substrate can easily be eliminated by choosing appropriate experimental geometry and substrate, eliminating the contribution of the surface carrying the thin film is not straightforward.[21] In addition, an important component of the bulk contribution to SHG is inseparable from the surface contribution in any experimental geometry.[22]

It is common to neglect all substrate contributions when they are expected to be much lower than the response of the nonlinear film. For molecules with weak second-harmonic response (such as TSe), the assumption is justified for sufficiently thick LB films but should be waived for thin films. In our calculation we deliberately used the same assumption with every film investigated to address the ability of the single- and two-beam arrangements to detect deviations between the theoretical model used and the actual experimental situation.

V. RESULTS AND DISCUSSION

The experimental coefficients of TSe/ODA LB films of various thicknesses were measured using both single- and two-beam polarized SHG arrangements and were used to calculate the susceptibility components of the films. Since the reflections from the front and back surfaces of the glass substrate were clearly separated, we neglected multiple reflections in the glass substrate in the theoretical model and just corrected the SHG field with the Fresnel transmission coefficient for the glass–air interface. As pointed out before, we also neglected all substrate contributions to the nonlinear response of the sample.

TABLE III. Results for the relative complex values of the susceptibility components obtained with the single-beam SHG arrangement.

Sample	*zxx*	*xxz*	*zzz*
70 layers TSe/ODA	1	$1.03+0.19i$	$17.66-0.77i$
50 layers TSe/ODA	1	$1.26-0.02i$	$16.92+6.24i$
20 layers TSe/ODA	1	$0.78-0.30i$	$12.09+4.47i$

Table III shows the single-beam results for the relative complex values of the susceptibility components. For a thick LB film of 70 layers, for which the response of the glass substrate can be neglected, the phase difference between the susceptibility components *zzz* and *zxx* is small, as expected. Nevertheless, the results still show a residual phase difference of approximately 10° between the *zxx* and *xxz* components. We verified by a numerical simulation that the susceptibility values calculated with the theoretical model are very sensitive to the measured expansion coefficients. In particular, the observed phase shift results from small errors in the imaginary part of the expansion coefficient h_s. Therefore, these results are a consequence of the limited precision of the single beam setup in determining the expansion coefficients of the sample.

In the single-beam setup, the precision of the expansion coefficients is limited by the high number of fitting parameters needed to describe a given signal. In addition, the setup requires the use of filters to spectrally separate the SHG signal and to block unwanted SHG light from the optical components. In principle, an isotropic filter oriented at normal incidence should not have any influence on polarization. However, commercial filters often present a small residual amount of stress-induced birefringence, which can change noticeably the polarization of a transmitted beam even when the filter is aligned at normal incidence. Such filters compromise the polarization purity of the arrangement, as we verified in a separate experiment.

For thinner LB films of 50 and 20 layers, the difference between the *zxx* and *xxz* components and the phase difference of the *zzz* component increase. For rodlike molecules (such as the one investigated), the results are clearly wrong, since Eq. (10) is not satisfied. However, for more complicated molecules in which the three nonvanishing tensor components can assume arbitrary complex values there would be no way of verifying whether the results obtained with the single-beam arrangement are correct.

The reason for the errors obtained for thin LB films is the contribution of the glass substrate to the nonlinear response, which was deliberately neglected in our theoretical model. Since plane substrates were used, the contributions from both surfaces of the substrate contribute to the measured signal. While the relative phase of the contributions from the film and from the first surface is fixed (depending

TABLE IV. Results for the relative complex values of the susceptibility components obtained with the two-beam SHG arrangement.

Sample	zxx	xxz, calculated neglecting h_s/k_s	zzz, calculated neglecting h_s/k_s
70 layers TSe/ODA	1	$1.03+0.03i/1.01-0.05i$	16.86−0.05i/16.97+0.05i
50 layers TSe/ODA	1	$1.04-0.12i/1.00-0.11i$	15.97+3.31i/16.24+3.28i
20 layers TSe/ODA	1	$0.94-0.61i/0.85-0.45i$	17.46+5.13i/18.47+3.96i
2 layers TSe/ODA	1	$1.14+0.84i/0.57-1.76i$	15.39−13.39i/17.83+12.26i
Glass substrate	1	$-2.77+0.05i/5.81-0.54i$	37.79−1.52i/−26.29+2.84i

on the susceptibility tensor), the relative phase of the contributions of the bulk and of the second surface of the glass depend on the exact thickness of each substrate (different for each sample). Such complicated interference effects have a dramatic impact on the measured signals for thin films.

The results for the susceptibility components obtained with the two-beam arrangement are presented in Table IV. For a thick sample of 70 layers, the components zxx and xxz of the susceptibility tensor are equal, and there are no phase differences between the susceptibility components. The results obtained with the two-beam setup are in qualitative agreement with those obtained with the single-beam setup, but are clearly more precise and better satisfy Eq. (10). The increased precision is a consequence of the simpler dependence of the measured signals on the expansion coefficients and of the fact that no spectral filters are necessary in the two-beam arrangement.

When the film thickness is reduced to 50 and 20 layers, the results progressively deviate from the expected values, as in the single-beam case. However, the two-beam arrangement offers a direct way of verifying whether the results obtained are consistent. Two independent solutions for the susceptibility components xxz and zzz can be obtained by neglecting f_s or g_s, respectively. For thick LB films, these two solutions are in excellent agreement (see Table IV). The consistency of the results is clearly compromised for thinner LB films, for which the response from the glass surface is relatively stronger. This consistency check is not available in the single beam setup.

To further investigate the possibilities offered by the two-beam setup, we measured the susceptibility components of a two-layer LB film of TSe/ODA (for which the signals from the film and from the glass surface are comparable) and those of a clean glass plate. The results for the clean glass plate were modeled by assuming that the nonlinear response arises from a very thin glass layer at the front surface of the plate. As clearly seen in Table IV, the solutions obtained by neglecting h_s or k_s are in complete disagreement, and therefore indicate that there are systematic errors in the experimental setup, or, alternatively, that the theoretical model used is incorrect.

The two-beam technique is very sensitive to the alignment of the fundamental beams and of the optical components used to control their polarization states (wave plates and polarizers). On the one hand, this requires some more care in the alignment as compared to the traditional single-beam arrangement. On the other hand, the sensitivity also serves as an indicator of a properly aligned setup.

VI. CONCLUSIONS

We demonstrated the advantages of polarized SHG using two fundamental beams for the characterization of thin films as compared to the more common single-beam arrangement. The technique allows precise determination of the relative values of complex experimental parameters and provides direct ways of verifying the internal consistency of the experimental data and of the calculated susceptibility components.

The superiority of the two-beam arrangement was demonstrated by determining the susceptibility tensors of LB films. We showed that the results obtained with the single- and two-beam SHG arrangements are in good agreement for a well-understood reference sample. In a more complicated experimental situation, however, the single-beam technique appears to work well but yields results that are, in fact, incorrect, whereas the two-beam technique yields internally inconsistent results, thereby highlighting systematic errors in the experimental arrangement or, alternatively, in the theoretical model.

Similarly to single-beam arrangements, the two-beam technique can be extended to measure the complex values of the susceptibility components with respect to a well characterized reference material by using interferometric methods and by exercising due care in the proper calibration of the results.[23] The advantages of two-beam polarized SHG can be easily extended to polarized SFG experiments, which are naturally performed in a noncollinear geometry.

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