

Determination of second-order susceptibility components of thin films by two-beam second-harmonic generation

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Received January 27, 2003

We measure the susceptibility components of a poled polymer film by second-harmonic generation with two beams at the fundamental frequency. The technique allows the consistency of experimental data and the validity of the theoretical model used to analyze the results to be addressed. Our results are in agreement with the expected values, provided that the linear optical properties of the sample are properly included.

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OCIS codes: 190.0190, 310.6860.

Second-harmonic generation (SHG) is a well-known method of investigating surfaces and interfaces in a variety of physical systems.^{1–3} Since it is a second-order nonlinear optical process, SHG is dipole forbidden in centrosymmetric materials. The centrosymmetry is inevitably lifted at a surface.³ By the same token, SHG is a sensitive probe of the orientational ordering of molecules in adsorbates or thin films deposited on a substrate.

SHG is described by the susceptibility tensor $\chi^{(2)}$, which is related to the macroscopic structure of the sample.³ We consider the common case of achiral thin films with in-plane isotropy but broken symmetry along the surface normal (symmetry $C_{\infty v}$). The tensor then has only three independent components, $\chi_{zzz}^{(2)}$, $\chi_{zxx}^{(2)}$, $\chi_{zyy}^{(2)}$, and $\chi_{xxz}^{(2)} = \chi_{yyz}^{(2)}$, where x and y are in the in-plane coordinates and z is the surface normal.

For samples consisting of rodlike molecules, whose molecular hyperpolarizability is dominated by a single tensor component β_{333} , the susceptibility tensor also yields information on the average orientation of the molecules.^{4–7} Neglecting local-field effects, one finds³

$$\begin{aligned}\chi_{zxx}^{(2)} &= \chi_{xxz}^{(2)} = \frac{1}{2} N \beta_{333} \langle \cos \theta \sin^2 \theta \rangle, \\ \chi_{zzz}^{(2)} &= N \beta_{333} \langle \cos^3 \theta \rangle,\end{aligned}\quad (1)$$

where N is the molecular number density, θ is the angle between the molecular axis and the surface normal, and the angle brackets indicate averaging over molecular orientations. Assuming a narrow orientational distribution, an average orientation angle can be calculated from the ratio $\chi_{zxx}^{(2)}/\chi_{zzz}^{(2)}$ without knowledge of the molecular nonlinearity.⁴

In general, the susceptibility tensor $\chi^{(2)}$ is not directly accessible in a nonlinear optical experiment and must be extracted from experimental data. This requires a suitable theoretical model and a number of independent measurements.⁸ Often, real-valued tensor components and the validity of Eq. (1) are implicitly assumed, and the average molecular orientation is obtained directly from a ratio of measured

SHG signals.^{4–7} This approach is justified in principle but has several limitations in practice. The SHG signals depend sensitively on the details of the experiment, such as the alignment of the optical elements and the linear optical properties of the sample. Moreover, for molecules with more than one hyperpolarizability component the measured signal ratio could be a consequence of a completely different orientational arrangement. Before conclusions are made about molecular orientation, the quality of the experimental data and the validity of the theoretical model should be addressed by determination of the complex values of all independent susceptibility components. In particular, one should verify that

$$\chi_{zxx}^{(2)} = \chi_{xxz}^{(2)} = \chi_{zzz}^{(2)}/a, \quad (2)$$

where a is a real number, as implied by the assumptions of rodlike molecules and azimuthal symmetry [Eq. (1)].

In this Letter we present a new technique for determining the complex-valued susceptibility components of thin films. The technique is based on detailed polarization measurements of the SHG response by use of two beams at the fundamental frequency. The use of the second beam reduces the number of nonlinear coefficients needed to describe any single SHG measurement and therefore improves the precision of their determination. The technique also allows the internal consistency of the experimental data to be addressed in a simple way. We apply the technique to measure precisely the nonlinear coefficients of a poled polymer film and then extract its susceptibility components by following a Green's-function approach.⁹ We show that the results are in agreement with the expected values, provided that the linear optical properties of the sample are properly included.

We consider the geometry of Fig. 1. Two beams (control and probe) at the fundamental frequency are applied to the same spot on the sample. SHG light produced jointly by the beams is detected in transmission. Expressing the fields as a sum of p (parallel to the plane of incidence) and s (perpendicular to it) components yields the components of the SHG signal from a sample of symmetry $C_{\infty v}$ in the form

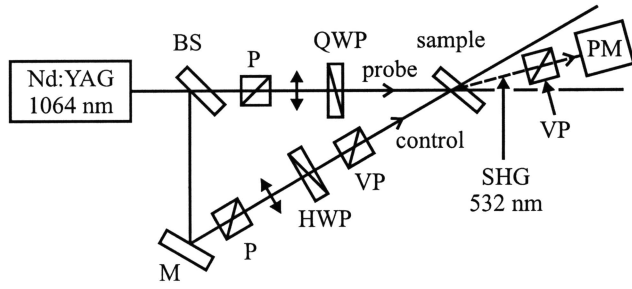


Fig. 1. Geometry for measuring the susceptibility components by two-beam SHG. BS, beam splitter; Ps, polarizers; QWP, quarter-wave plate; HWP, half-wave plate; M, mirror; VPs, variable-angle polarizers; PM, photomultiplier tube.

$$E_p(2\omega) = f_p A_p(\omega) B_p(\omega) + g_p A_s(\omega) B_s(\omega), \quad (3)$$

$$E_s(2\omega) = f_s A_p(\omega) B_s(\omega) + g_s A_s(\omega) B_p(\omega), \quad (4)$$

where A and B are the amplitudes of the incident control and probe beams, respectively. Equations (3) and (4) are defined with respect to the fundamental and SHG field amplitudes outside the sample, because these are the only fields that can be controlled experimentally. The expansion coefficients f_i and g_i in Eqs. (3) and (4) are linear combinations of the susceptibility components. They depend on the linear optical properties of the sample and on the experimental geometry. Nevertheless, the coefficients fully describe the nonlinear response of the sample for arbitrary input polarizations of the fundamental beams and are the quantities that can be measured most directly in an experiment.

The expansion coefficients f_i and g_i of a sample are determined by detailed polarization measurements of the sample's nonlinear response. In particular, we measure the dependence of the intensity of the joint SHG signal on the polarization of the probe beam while keeping the polarization of the control beam fixed. Because all measurements are performed on a relative scale, one of the expansion coefficients can always be normalized to 1. Different combinations of fundamental and signal polarizations (Table 1) permit the determination of the relative values of all four coefficients in Eqs. (3) and (4) without the need to calibrate absolute signal levels. A given expansion coefficient can be calculated from the set of measurements presented in Table 1 in two independent ways, which allows the internal consistency of the data to be verified. At this stage, inconsistency in the determined coefficients indicates a misalignment in the experimental setup or a sample with symmetry lower than $C_{\infty v}$.

We note that polarization techniques are also applicable to the more common situation where only one fundamental beam is used. To avoid the need to calibrate absolute signal levels in such experiments, one needs to mix the p and s polarization components of the SHG signal in detection. This results in SHG signal intensities that depend simultaneously on the

relative values of three complex expansion coefficients and are therefore not always very sensitive to small changes in the coefficients' values. The new two-beam arrangement offers a possibility for overcoming this problem. When the polarization of the control beam is fixed, Eqs. (3) and (4) imply that any SHG signal produced jointly by the two fundamental beams is specified by only two complex parameters. Such simple dependence significantly improves the precision in the determination of the expansion coefficients.

The nonlinear material used in this work was the side-chain polymer A-095.11 (Sandoz). In this material the chromophores have a strong nonlinearity along the charge-transfer axis, and their hyperpolarizability is dominated by a single component. Equations (1) and (2) are therefore expected to be valid. A thin film of the polymer was obtained by spin coating onto a glass substrate, which was then electrically poled (corona poling) to introduce a net alignment of the chromophores while maintaining in-plane isotropy ($C_{\infty v}$ symmetry). The film had a thickness of 250 nm and a principal absorption maximum at 502 nm.

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 SHG. With a single fundamental beam the SHG signal was measured to be independent of the rotation angle of the film about its surface normal, indicating in-plane isotropy of the sample. To determine the nonlinear coefficients of the film, we split the fundamental beam into two beams of nearly the same intensity (control and probe), which were applied to the same spot of the film with incident angles of 40.3° and 52.8°, respectively (Fig. 1). The beams were focused to achieve sufficient separation of their reflections from the front and back surfaces of the glass substrate. A photomultiplier tube was used to detect SHG light at 532 nm produced jointly by the beams.

The control beam was linearly polarized with a calcite Glan polarizer (extinction ratio $\sim 4 \times 10^{-6}$). A given polarization component of the SHG signal was then recorded while the relative amplitude and phase of the probe field components were continuously varied by means of a rotating quarter-wave plate.¹⁰ The polarization of the control beam was kept fixed during the measurement; therefore each recorded polarization line shape could be described by only two expansion coefficients (Table 1). By normalizing to $f_p = 1$, we obtained $g_p = 0.221 - 0.029i$, $f_s = 0.268 + 0.001i$, and $g_s = 0.340 - 0.016i$, with an overall accuracy of approximately 1%.

Table 1. Possible Choices of Control and Signal Polarizations

Control Polarization	Signal Polarization	Determined Coefficients
p	$\pm 45^\circ$	f_p, f_s
s	$\pm 45^\circ$	g_p, g_s
$\pm 45^\circ$	p	f_p, g_p
$\pm 45^\circ$	s	f_s, g_s

This precise set of expansion coefficients establishes a firm starting point for a successive calculation of the susceptibility components. The linear optical properties of the film at the fundamental and SHG frequency must be taken into account in calculating the fundamental fields inside the thin film and the actual SHG field that exits the multilayer geometry. To extract the susceptibility components from the expansion coefficients, we used a model based on the Green's-function formalism,⁹ including refraction, multiple reflections, and propagation effects for the fundamental and SHG beams.

The values obtained for the susceptibility components depend sensitively on the details of the theoretical model used to describe the experiment. To investigate the role of the linear properties of the sample, we first calculated the susceptibility components by assuming that the refractive index of the film was the same as that of the ambient medium (air) or the substrate (BK7). Such approximations are widely used for investigating the nonlinear response of single molecular layers or of interfaces between two isotropic media.⁴⁻⁷ By normalizing to $\chi_{xxx}^{(2)} = 1$, we obtained approximately $\chi_{xxz}^{(2)} = 1.3 - 0.3i$ and $\chi_{zzz}^{(2)} = 2.7 - 2.3i$ in the first case and $\chi_{xxz}^{(2)} = 1.3 + 0.1i$ and $\chi_{zzz}^{(2)} = 5.3 + 1.4i$ in the second. These results are clearly in disagreement with Eq. (2).

When the correct values for the refractive indices (1.676 at 1064 nm and $2.298 + 0.176i$ at 532 nm) were used, the procedure yielded $\chi_{xxz}^{(2)} = (1.03 + 0.03i) \pm (0.04 + 0.04i)$ and $\chi_{zzz}^{(2)} = (3.8 + 0.4i) \pm (0.6 + 0.5i)$. The value of $\chi_{zzz}^{(2)}$ was found to be sensitive to the parameters used in the model and could be determined with precision lower than $\chi_{xxz}^{(2)}$. Such sensitivity arises from the complicated dependence of $\chi_{zzz}^{(2)}$ on the experimental expansion coefficients. The results are nevertheless in good agreement with Eq. (2). For samples poled in a moderate electric field¹¹ the constant a in Eq. (2) is expected to be 3. However, higher values of a are sometimes observed, especially in the case of corona poling.^{12,13} We also verified the importance of the small imaginary parts of the experimentally determined expansion coefficients f_i and g_i . When they were neglected, we obtained a value of $\chi_{xxz}^{(2)} = (1.06 - 0.10i) \pm (0.04 - 0.04i)$.

In conclusion, we have demonstrated a technique based on two-beam SHG for determining the nonvanishing susceptibility components of thin films. The technique allows the consistency of experimental data and the validity of the theoretical model used to describe the results to be addressed. The use of the second beam reduces the number of nonlinear coefficients needed to describe any single SHG measurement and therefore improves the precision of their determi-

nation, compared with the simple case when only one fundamental beam is used. A direct comparison of the one- and two-beam techniques will be the subject of future experiments. The new two-beam technique allows the complex relative values of the nonvanishing susceptibility components to be measured precisely. The technique can easily be extended to measure the absolute magnitude of the susceptibility components by using a well-characterized material as a reference and by exercising due care in the proper calibration of the results, as must also be done when the one-beam technique is used.

Particularly promising is the future application of the technique to the study of molecular layers adsorbed on surfaces. In the theoretical treatment of such samples there are still open questions as to how to include the linear properties of the molecular layer. Most works are based on a widely adopted phenomenological model that neglects the linear properties of the active layer. We believe that our technique will allow these important issues to be addressed.

We acknowledge support for this work from the Academy of Finland (53961). The poled polymer sample was provided by O. Zehnder and P. Günter. We also thank L. Ylinen for technical assistance. S. Cattaneo's e-mail address is stefano.cattaneo@tut.fi.

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