COMMUNICATIONS

A regression technique to analyze the second-order nonlinear optical response of thin films

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We present a new technique, based on regression analysis, to determine the second-order nonlinear optical susceptibility tensor of thin films. The technique does not require the absolute levels or phases of measured signals to be mutually calibrated. In addition it yields indicators that address the quality of theoretical models describing the sample. We use the technique to determine the susceptibility tensor of samples of a nonracemic chiral material which have very low symmetry (both chiral and anisotropic) and have many independent tensor components. The results show the importance of using detailed theoretical models that account for the linear optical properties of the sample. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1767151]

Second-order nonlinear optical processes depend strongly on material symmetry. For example, inversion symmetry forbids any second-order effects within the electric-dipole approximation. At interfaces, the symmetry is easily broken, which makes second-order techniques sensitive probes of the structures and properties of surfaces and thin molecular films.[1–3] In particular, the structure of the second-order susceptibility tensor $\chi^{(2)}$, the fundamental quantity describing the nonlinear response of the sample, is determined by the symmetry of the sample.[4]

The susceptibility tensor itself cannot be measured directly but must be extracted from experimental data with the aid of a theoretical model. For thin films of low symmetry, this can be very complicated because the tensor has many complex-valued nonzero components, and therefore, results from several independent measurements must be combined. Nevertheless, only precise information about the susceptibility tensor allows definitive conclusions to be made about the structure of the sample, such as separating chiral and anisotropic contributions to the nonlinearity[5] or addressing the molecular and structural origins of the chiral nonlinearity.[6,7]

In a typical thin-film geometry for second-harmonic generation (Fig. 1), the intensity of the detected second-harmonic field can be expressed as[8]

$$I(2\omega)=|fE_p^2(\omega)+gE_s^2(\omega)+hE_p(\omega)E_s(\omega)|^2, \qquad (1)$$

where E_s and E_p are the *s*- and *p*-polarized (perpendicular and parallel to the plane of incidence, respectively) components of the fundamental beam at frequency ω. The expansion coefficients *f*, *g*, and *h* are in general complex-valued and associated with the various quadratic combinations of the components of the fundamental field and are the quantities whose relative values can be uniquely determined for each measured signal in an experiment.[9] Theoretically, the coefficients are linear combinations of the components of the second-harmonic susceptibility tensor that depend on the experimental geometry and the level of sophistication used in the theoretical modeling.[8]

Using the experimental coefficients *f*, *g*, and *h* from a number of different measurements to determine the components of the susceptibility tensor raises several problems. In particular, each measurement yields only the relative values of the complex coefficients for that measurement. The absolute signal levels of different measurements may differ for various reasons.[10] Even if the signal levels were somehow fully calibrated, a phase uncertainty between the coefficients of different measurements would remain. Interferometric phase measurements[11] require very high stability, which is extremely difficult to maintain if the sample needs to be repositioned between independent measurements. A more practical problem is that the precision with which the coefficients *f*, *g*, and *h* are measured may vary. Furthermore, the choice of the theoretical model will also influence the final results. The most complete models[12] are tedious to implement and various approximations are often used without proper justification. Usually, the final results do not allow the quality of the model to be estimated.

In this paper, we present a regression-based technique to

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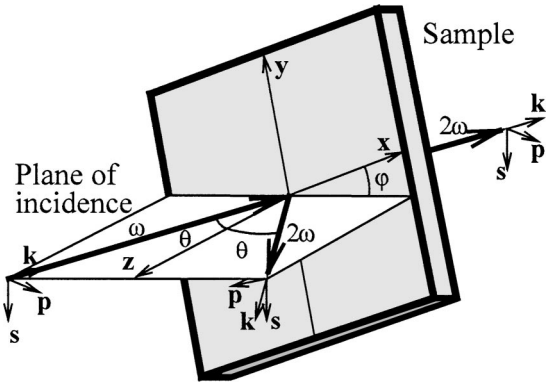

FIG. 1. A schematic of the experimental geometry used to determine the second-harmonic susceptibility of thin film samples. A fundamental beam of frequency ω traveling in **k**-direction is incident on the thin film at angle θ. Coherent second-harmonic light at frequency 2ω is emitted in the transmitted and reflected directions. All beams can be expanded in terms of their *p*- and *s*-components. The xyz-coordinate system, in which the susceptibility $\chi^{(2)}_{ijk}$ is expressed, is fixed with respect to the sample. The orientation of the sample is characterized by the azimuthal angle φ.

determine the second-harmonic susceptibility tensor of thin films. The technique does not require absolute calibration of signal levels or phases, improves the precision of the final results through weighted use of many measurements of varying accuracy, and allows the quality of different theoretical models describing the sample to be assessed. We demonstrate the technique by determining the susceptibility tensor of a thin film that has very low symmetry due both to anisotropy in the plane of the film and chirality.

We consider a geometry schematically shown in Fig. 1. The fundamental beam (frequency ω) is incident on a thin film at angle θ. Second-harmonic beams (frequency 2ω) generated by the film are detected in the transmitted and/or reflected directions. The susceptibility tensor $\chi^{(2)}_{ijk}$ is expressed in a Cartesian coordinate system ijk attached to the sample with z along the sample normal and x and y the in-plane coordinates. The orientation of the sample in the arrangement is defined through the azimuthal angle φ between the x direction and the plane of incidence.

The relative values of the complex expansion coefficients *f*, *g*, and *h* in Eq. (1) for a given second-harmonic signal can be determined experimentally by using a continuously-rotating quarter-wave plate to manipulate the polarization of the incoming field.[9] To determine the values of the nonvanishing components of the susceptibility tensor, the number of independent measurements must be sufficient compared to the number of unknown tensor components. For samples of low symmetry, which have several independent tensor components, the experimental geometry must be varied to increase the number of independent measurements. In the case of in-plane anisotropy, this is achieved by performing measurements at different azimuthal orientations φ.

To avoid problems arising from the uncalibrated levels and phases of different signals, a complex scaling factor c_i is introduced for each measurement.[5,13] The factors adjust the sets of *f*, *g*, and *h* coefficients (and the resulting tensor components) to a common scale and phase. The scaled values of the expansion coefficients obtained from the *i*th measurement are then equated to the corresponding theoretical expressions as follows:

$$\begin{aligned} f_i^t &= c_i f_i^m, \\ g_i^t &= c_i g_i^m, \\ h_i^t &= c_i h_i^m, \end{aligned} \tag{2}$$

where the superscript m denotes the measured values. The theoretical expressions denoted by the superscript t are of the form

$$f_i^t = \sum_{j=1}^{q} a_{ij} \chi_j \tag{3}$$

with the theoretical coefficients a_{ij} and the number of independent susceptibility components q determined by the experimental geometry and the theoretical model. The whole procedure results in a set of linear equations in which the tensor components and scaling factors are the unknowns.

In the most straightforward application of the procedure, one matches the number of measured coefficients with the number of unknown quantities. This procedure neatly gives a solution for the susceptibility components, but any information concerning the validity of this solution must be obtained by other means. In addition, the measured signals are not always sensitive to small variations in the values of the expansion coefficients, which compromises the precision of their determined values. We reduce the relative importance of the individual measurements by increasing their number well beyond the number of unknown quantities. Essentially, this results in an over-determined set of linear equations. We solve it using total least squares regression,[14] where weighting may be used to compensate for the possibly different accuracies of the measurements. The solution yields the relative values of the susceptibility components and the scaling factors.

The regression procedure also provides indicators that can be used to assess the quality of the final results. In particular, the residuals of the total least squares solution describe how much the theoretical and experimental expansion coefficients differ. All theoretical models describing samples of same symmetry have the same number of independent susceptibility components but the values of the coefficients a_{ij} in Eq. (3) depend on the models' level of detail and the measurement data. If the data were perfectly free from noise and measurement errors, a perfectly matching theoretical model would produce complete congruity among all equations so that the residuals would all vanish. Any imperfections in the model lead to incorrect theoretical description of the experiment. Therefore, despite having perfect data, only an approximate regression solution can be found when the number of equations exceeds that of the unknowns, which results in nonvanishing residuals. The worse the model, the larger the residuals.

In practice, the measurements inevitably contain at least some noise. However, if different theoretical models are compared using the same measurement data, the residuals provide a direct indication of the quality of the theoretical model for a given set of data.

In addition to the susceptibility components, the solution contains the complex scaling factors c_i. Since for homogeneous samples the factors should have nearly equal magnitudes for measurements performed using the same fundamental beam intensity, their values provide an independent indicator of the quality of the theoretical model describing the sample.

To demonstrate the new procedure, we used Langmuir–Blodgett (LB) films of a tetradodecyloxyhelicenebisquinone.[15] Materials of this family are known to form LB-films of high quality, which are chiral and anisotropic belonging to the symmetry group C_2.[16] Due to their complicated structure, such samples are ideally suited to test our new measurement technique.

The only symmetry operation for the samples is a 180° rotation about the sample normal.[5,17] Thus the directions of the in-plane axes cannot be fixed by any symmetry operation. Nevertheless, the *y*-axis was chosen to be along the dipping direction of the film during the LB deposition. The samples used had a film on one side of the substrate only. The 1064-nm output of a Q-switched Nd:YAG laser provided the fundamental beam (~10 ns pulse length, 30 Hz repetition rate, ~1 mJ pulse energy), which was weakly focused to a diameter of ~0.5 mm at the sample and was incident at an angle of 45°. Second-harmonic light from the optical components preceding the sample was carefully filtered out. The transmitted second-harmonic light (532 nm) generated by the sample was filtered appropriately before it was detected using a photomultiplier tube, a digital oscilloscope, and a computer. The signals were recorded while the polarization of the fundamental beam was varied[9] by a computer-controlled quarter-wave plate rotated through 360°. The procedure was repeated at different azimuthal orientations of the sample.

The results were analyzed using two theoretical models based on the electric-dipole approximation and symmetry group C_2. Although the second-order response of chiral thin films may have significant magnetic-dipole contributions,[13,18] previous work on similar helicenebisquinones suggests that such higher-order contributions are not important.[5] The first model is very detailed and accounts for the linear optical properties and the thickness of the sample as well as multiple reflections and refraction at the interfaces.[12] Such models are well understood but, unfortunately, tedious to implement. Therefore the linear optical properties and thickness of the film are often neglected. This is done in a second, simplified, model, which assumes that the index of refraction of the film is unity and that its thickness is negligible.

The simple model can be evaluated analytically.[5] The detailed model was evaluated numerically using the estimated values of 1.5 and 1.6 for the indices of refraction of the film at the fundamental and second-harmonic wavelengths, respectively, and a thickness of 1.95 nm per molecular layer. The index of refraction of the substrate was taken to be 1.52. These numbers are approximate and based on earlier results on similar materials.[19] However, our conclusions do not depend on the exact values of these quantities.

The relative values of the independent tensor components for a 16-layer sample determined using the two models are shown in Fig. 2. The measurements were performed for 18 different azimuthal orientations φ of the sample detecting both *s*- and *p*-polarized signals, yielding 90 independent expansion coefficients. This number greatly exceeds the number of unknown quantities (43; 36 scaling constants and eight independent tensor components, of which one can be scaled to unity). The relative weight of each equation in the regression problem was assigned according to the uncertainties in the determined *f*, *g*, and *h* coefficients. The results of the two models are qualitatively similar showing the importance of both chirality and anisotropy in the nonlinear response. For samples with in-plane isotropy, $xyz=-yxz$ and $zxy=0$,

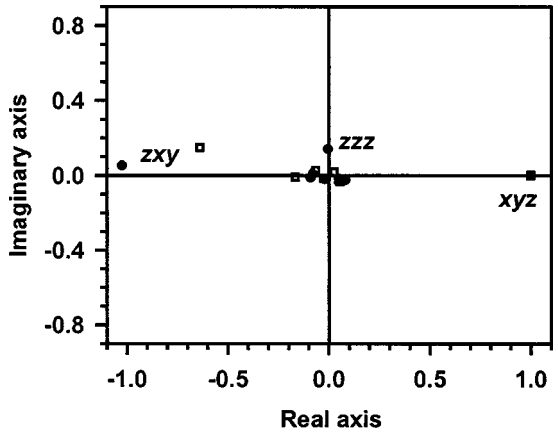

FIG. 2. The values of the independent susceptibility components obtained for a thin film sample of helicenebisquinone molecules using the two models: simple (open square) and detailed (dot). The small components, including *zzz* of the simple model, are not labeled.

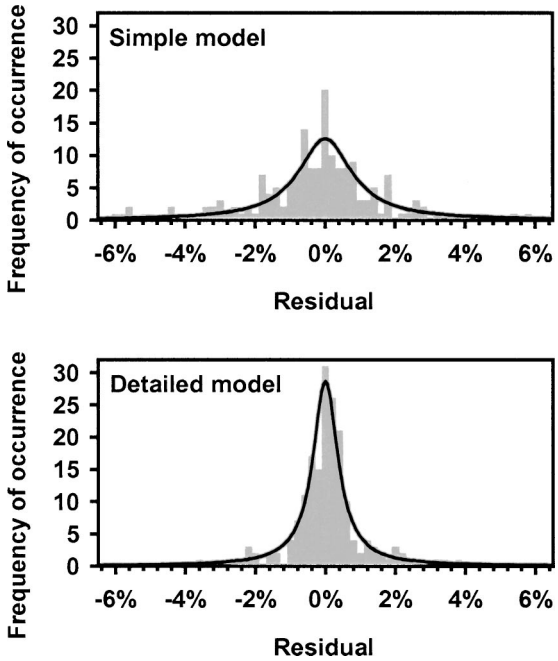

FIG. 3. Histogram bar plots (bin width 0.2%) of the residuals of the regression solutions for the two theoretical models: simple (above) and detailed (below). Contour lines and common scale are used to facilitate the comparison of the plots. Standard deviations of the distributions are 2.5% (simple) and 1.0% (detailed). Wider distribution of residuals indicates less accurate solution.

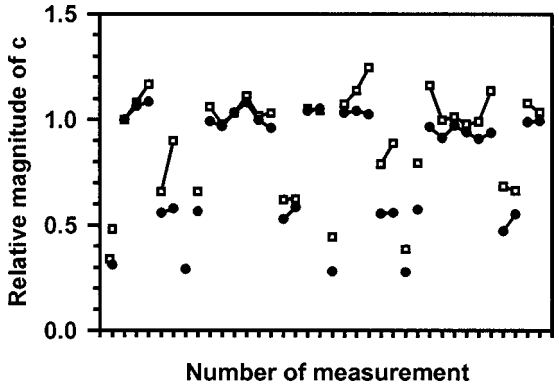

FIG. 4. Magnitudes of the solved values of the scaling factors c_i for the two models: simple (open square) and detailed (dot). The values expected to be equal assuming a perfect sample are indicated by connecting them with straight lines.

which clearly do not hold. The chiral and achiral contributions to the nonlinearity can only be discussed in terms of the combinations of components which do not depend on the choice of the orientation of the in-plane axes.[5,17] The combination $xyz-yxz$, which is associated with chirality, is clearly dominant as the achiral combinations zzz, $zxx+zyy$, and $xxz+yyz$ are very close to zero. In addition, the large component zxy is associated with both anisotropy and chirality.

The residuals of the regression solutions, shown in Fig. 3, on the other hand, reveal significant differences between the models. The residuals of the detailed model are much smaller, on the average, than those of the simple model, despite the equal number of unknowns in the two models. This indicates that the detailed model is much more accurate and shows the importance of including all the physical factors in describing the results.

Certain sets of measurements were performed in succession at the same laser intensity. For samples of high quality, the scaling factors for such measurements are expected to be equal in magnitude. This is evident in Fig. 4, which shows the magnitudes of the scaling factors for the two models. Again, the agreement within a given set is best when the detailed model is used.

Our results agree qualitatively with previous work on similar materials,[5,17,20] i.e., the response is dominated by chirality. However, our results for the quantitative values of the susceptibility components and their isotropic combinations differ significantly from those of Ref. 20 where the same material and similar Y-type LB-films were investigated. Such differences may be particularly important when different origins of the nonlinear response are considered. We believe that the results of the regression technique are more reliable as it allows several potential problems of earlier techniques to be avoided.

In conclusion, we have developed a new technique to determine the second-harmonic susceptibility tensor of thin films. The technique uses regression analysis and does not require the absolute levels or phases of measured signals to be calibrated. It weights different measurements according to their accuracy to improve the precision of the results and allows the quality of different theoretical models describing the sample to be assessed. We have demonstrated the technique using samples of C_2 symmetry, but the technique can be applied to other symmetry groups as well. The results show the importance of using detailed theoretical models that account for the linear optical properties of the sample.

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