Determining the values of second-order surface nonlinearities by measurements with wave plates of different retardations

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We measured the second harmonic generation response of a thin film consisting of chiral molecules with four wave plates having different retardation coefficients. By means of the fitting procedure described in a previously reported formalism, we demonstrated that a single set of tensor components of second order surface nonlinearities fits all the data. Our results provide clear experimental evidence for the validity of this method, which can find applications in the studies of chiral structures and achiral anisotropic materials. © 2009 Optical Society of America

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1. Introduction

Chirality is the geometric property of a rigid object (or spatial arrangement of points or atoms) of being nonsuperposable on its mirror image. Many of the molecules that are important in nature are chiral, and, consequently, there is a great interest in experimental techniques capable of distinguishing between left- and right-handed forms of compounds.

Due to its high sensitivity to symmetry breaks in materials, optical second harmonic generation (SHG) has been demonstrated to be a very good tool for studying chirality from a surface composed of left- or right-handed molecules [1]. In fact, based on this nonlinear optical technique, several methods have been developed, such as second harmonic generation circular dichroism (SHG-CD) [2,3], second harmonic generation linear dichroism (SHG-LD)[4], and second harmonic generation optical rotatory dispersion (SHG-ORD) [5], which all exhibit sensitivities orders of magnitude larger than their linear counterparts. The quantities measured in each of these methods depend on a given set of tensor elements from the first order nonlinear optical susceptibility. Measuring the values of all of these tensor elements characterizes completely the second harmonic optical response of the sample. The most practical way of obtaining a complete picture of these tensor elements is by using a quarter-wave plate in order to manipulate the polarization state of the incoming fundamental light [6].

With the advent of tunable femtosecond lasers and the associated optical parametric amplifiers, it has become possible to study SHG at different wavelengths. With respect to chirality, SHG spectra are very interesting, as they allow a comparison with linear optical absorption spectra and therefore the investigation of the properties in and out of resonances. To this purpose, a theoretical approach has been proposed, stating that it is possible to obtain the correct value for the tensor components with a wave plate of any retardation (other than a half-wave plate) [7]. The direct consequence of this statement is that a single wave plate is sufficient to measure the spectral dispersion of the tensor components, as long as the retardation is known for each wavelength. Hence one could avoid the use of expensive

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photo-elastic or electro-optic modulators or the use of Berek or Soleil–Babinet compensators, which require specific adjustments for each wavelength. However, to our best knowledge, there has been no experimental support so far for this model.

In this paper, we provide experimental evidence for the validity of the above-mentioned theoretical report. To this purpose, we measured the SHG response of a thin film consisting of chiral molecules, with four wave plates having different retardation. By means of the fitting procedure described in Ref. [6], we show that a single set of tensor components fits all the data. Possible applications of this method to the study of achiral anisotropic materials is subsequently discussed.

2. Experiments

The experiments were performed with a Ti:sapphire laser system (Mai-Tai, from Spectra Physics–Newport), which provides femtosecond pulses (120 fs) at 800 nm with a repetition rate of 80 Mhz, yielding high peak intensity at low average power; see Fig. 1. Since the laser output is polarized, we adjusted the beam intensity by a combination of a half-wave plate and a Glan–Thompson polarizer (GTP-M10, from Meadowlark). Subsequently, the polarization of the electromagnetic radiation was manipulated by a wave plate of a different retardation for all the experiments. This wave plate was mounted on an automatic rotation stage (m-urm100acc, from Newport), which was driven by a motion controller (ESP300, from Newport). Further on along the beam path, a lens with focal length of 200 mm focused the beam onto the sample, through a visible light filter that blocked the visible part of spectrum, while transmitting 90% of the infrared radiation. The sample holder was mounted in such a way that the angle of optical incidence was 45° on the specimen. Afterwards, an analyzer (also GTP-M10, from Meadowlark) enabled us to select SHG output with a specific polarization. Part of the beam was directed toward a photodiode (63476, from Hamamatsu), which was connected to the analog voltage input of a lock-in amplifier (SR530, from Stanford Research Systems), in order to monitor the intensity of the fundamental beam. The same lock-in amplifier was used to detect the SHG signal, and, for this purpose, the light intensity of the beam was modulated at 750 Hz by means of an optical chopper (SR540, from Stanford Research Systems). Following the chopper, a 400 nm bandpass filter (BG39, from Schott) ensured that only the photons at the double frequency from the fundamental were allowed through. Next, a lens focused the beam on the photomultiplier tube (XP2020, from Philips). Then, before reaching the lock-in amplifier, the electrical signal was preamplified 100 times, while, simultaneously, undesired high (>3 kHz) and low (<100 Hz) frequencies were eliminated with the two roll off filters of a preamplifier (SR560, from Stanford Research Systems). The obtained data were recorded with a LabView program on a personal computer.

The sample was a Langmuir–Blodgett thin film (y deposition, 300 layers) of an enantiomerically pure chiral helicene, deposited on a glass substrate. The structure of the molecules is shown in the inset of Fig. 1 [8,9].

3. Theoretical Introduction

The intensity of the second harmonic light along the S and P directions of polarization can be expressed in terms of the S and P components of the fundamental electric field $\mathbf{E}(\omega)$ as

$$I_{S,P}(2\omega) = |f_{S,P}\mathbf{E}_P^2(\omega) + g_{S,P}\mathbf{E}_S^2(\omega) + h_{S,P}\mathbf{E}_P(\omega)\mathbf{E}_S(\omega)|^2, \quad (1)$$

where the coefficients $f_{S,P}$, $g_{S,P}$, and $h_{S,P}$ are complex parameters, which are linear functions of the first order nonlinear susceptibility tensor elements. In the

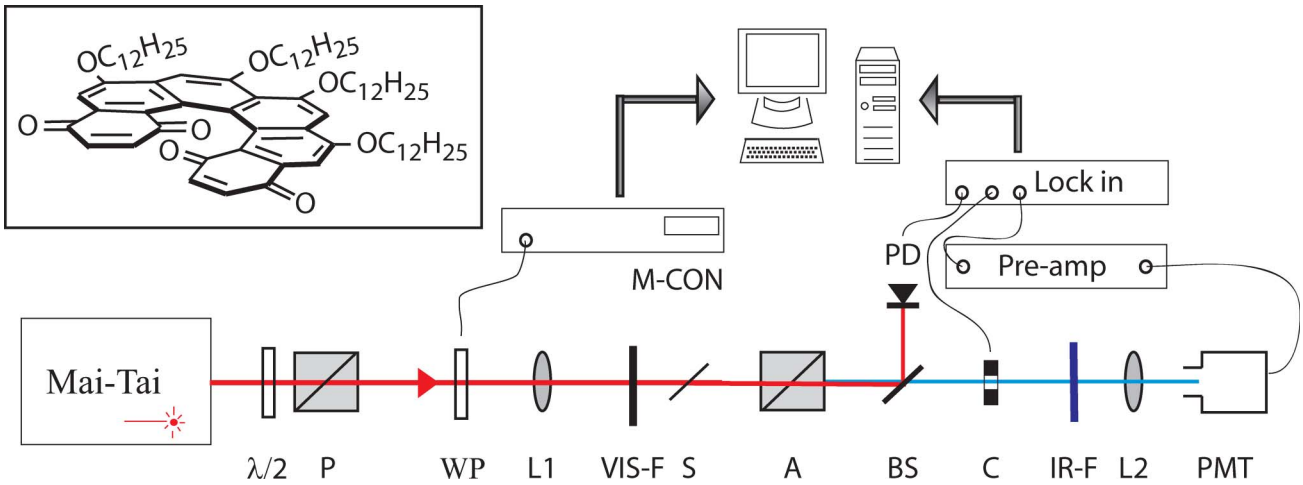

Fig. 1. (Color online) Schematic diagram of the experimental setup: $\lambda/2$, half-wave plate; P, polarizer; WP, wave plate; L1 and L2, lenses; VIS-F, visible light filter; S, sample; A, analyzer; BS, beam splitter; C, chopper; PD, photodiode; IR-F, infrared filter; PMT, photomultiplier tube; M-CON, motion controller. The inset shows the chemical structure of the sample, a chiral helicene molecule.

following, we indicate the real and imaginary parts of these complex numbers by the indices 1 and 2, respectively. The exact form of these coefficients depends on the symmetry of the sample. Furthermore, they are different for the reflected and transmitted second harmonic light, and they also depend on the angle of optical incidence.

Plotting the SHG intensity as a function of wave-plate angle allows one to extract the values of $f_{S,P}$, $g_{S,P}$, and $h_{S,P}$. For a wave plate of retardation δ (where $\delta = \pi$ is a half-wave plate and $\delta = \pi/2$ is a quarter-wave plate), the fitting formula for the second harmonic intensity as a function of the state of polarization of the incoming beam, which determined by the rotation of an angle θ_{WP} of the wave plate, can be expressed by [7]

$$\begin{aligned} I(2\omega) = A\Bigg\{ & \frac{1}{4}\Bigg[(f_1+g_1)\sin^2\frac{\delta}{2} - 2f_1\cos^2\frac{\delta}{2} \\ & - 4f_2\cos\frac{\delta}{2}\sin\frac{\delta}{2}\cos 2\theta_{\mathrm{WP}} \\ & + (f_1-g_2)\sin^2\frac{\delta}{2}\cos 4\theta_{\mathrm{WP}} \\ & + h_1\sin^2\frac{\delta}{2}\sin 4\theta_{\mathrm{WP}}\Bigg]^2 \\ & + \frac{1}{4}\Bigg[(f_2+g_2)\sin^2\frac{\delta}{2} - 2f_2\cos^2\frac{\delta}{2} \\ & + 4f_1\cos\frac{\delta}{2}\sin\frac{\delta}{2}\cos 2\theta_{\mathrm{WP}} \\ & + (f_2-g_2)\sin^2\frac{\delta}{2}\cos 4\theta_{\mathrm{WP}} \\ & + 2h_1\cos\frac{\delta}{2}\sin 2\theta_{\mathrm{WP}}\Bigg]^2\Bigg\}. \end{aligned} \tag{2}$$

In this equation, we have omitted the S and P indices for clarity of the notation. The coefficient A is simply a multiplication factor.

Depending on the way a particular wave plate is conceived and on the materials from which it is made, its retardation at wavelengths other than the one for which it is specified will differ. For the particular order of optical components described in Fig. 1, where we have a polarizer, a wave plate of "unknown" retardation, and an analyzer, the general form of the S and P components of the fundamental field is given by

$$\begin{aligned} \begin{bmatrix} \mathbf{E}_P(\omega) \\ \mathbf{E}_S(\omega) \end{bmatrix} = & \begin{bmatrix} \cos^2\beta & \cos\beta\sin\beta \\ \cos\beta\sin\beta & \sin^2\beta \end{bmatrix} \\ & \times \begin{bmatrix} \cos\frac{\delta}{2} + i\sin\frac{\delta}{2}\cos 2\theta & i\sin\frac{\delta}{2}\sin 2\theta \\ i\sin\frac{\delta}{2}\sin 2\theta & \cos\frac{\delta}{2} - i\sin\frac{\delta}{2}\cos 2\theta \end{bmatrix} \\ & \times \begin{bmatrix} \cos\alpha \\ \sin\alpha \end{bmatrix}, \end{aligned} \tag{3}$$

where $\theta = \theta_{\mathrm{WP}} + \theta_0$, θ_0 being the offset angle between the fast axis of polarization of the wave plate with respect to the P direction of polarization, while α and β are the angles of the polarization with respect to the planes of optical incidence of the polarizer and the analyzer, respectively. It can then be shown that, for $\alpha = \beta = 0$, the intensity of the fundamental light as a function of the angle of rotation of the wave plate is given by

$$I_P(\omega) = \cos^2\frac{\delta}{2} + \sin^2\frac{\delta}{2}\cos^2 2(\theta_{\mathrm{WP}} + \theta_0), \tag{4}$$

which, after fitting, yields the value of the retardation δ.

4. Results and Discussion

In Fig. 2, the intensity of the fundamental light at 800 nm is plotted as function of the wave-plate angle for four wave plates of different retardation at this wavelength. The wave plates had the following specifications: a quarter-wave plate at 1064 nm, a half-wave plate at 1064 nm, a reference quarter-wave plate at 800 nm, and a quarter-wave plate at 532 nm. The open signs correspond to the experimental data and the lines to fits with Eq. (4).

From these fits the retardations and offset angles are given in Table 1. The values for θ_0 vary since, in

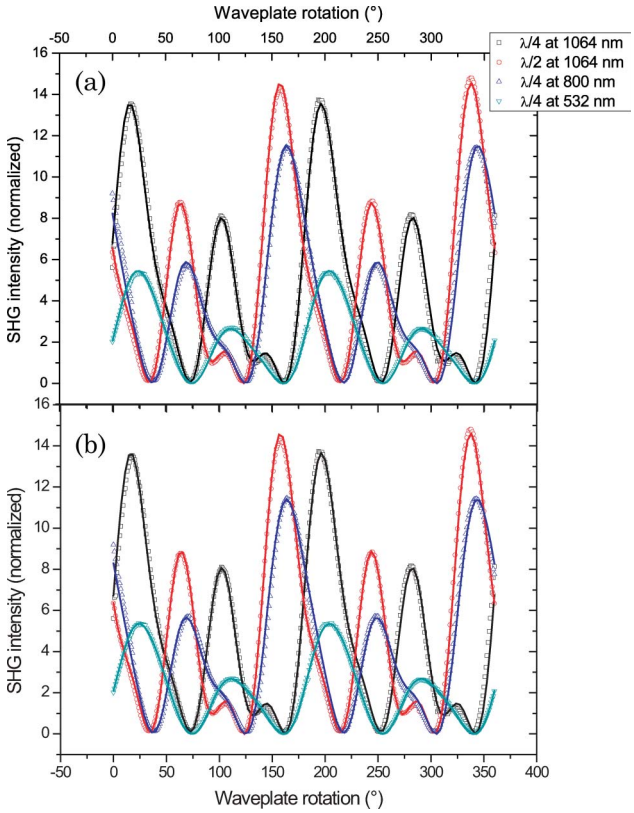

Fig. 2. (Color online) Intensity of the fundamental light at 800 nm versus the angle of rotation of four different wave plates. The experimental data are indicated with open symbols, and the lines correspond to theoretical fits.

Table 1. Fitting Parameters from the Fits in Fig. 2

	$\lambda/4$ at 1064 nm	$\lambda/2$ at 1064 nm	$\lambda/4$ at 800 nm	$\lambda/4$ at 532 nm
δ	2.07	−2.11	−1.57	1.08
θ_0	−17.5°	34°	37°	−16°

order to further test the fitting procedure, we inserted the wave plates at a random angular position.

In Fig. 3, the intensity of the second harmonic at 400 nm signal is plotted as function of the wave-plate angle for all four wave plates. Each SHG curve was divided by the square of the maximum intensity for the corresponding fundamental pattern in order to normalize the data. The experimental results are indicated by the open symbols, while the lines correspond to fits with Eq. (2). For the fitting procedure, we set as fixed the values in Table 1, while the values for f_1, f_2, g_1, g_2, and h_1 were fitted independently. Note that here again we omitted the subscript P for clarity of the notations. In order to set the phase between these components, we chose $h_2 = 0$. All the fitting coefficients are presented in Table 2. The error bars given are the ones yielded by the fitting program in OriginPro.

As can be seen from the values in Table 2, for the fits in Fig. 3(a), the sets of complex $f_{S,P}$, $g_{S,P}$, and $h_{S,P}$ parameters, which can be extracted from data recorded with "imperfect" wave plates, are approximately the same, although some divergence can be observed for the smallest quantities, which is probably due to noise in the experimental data points.

In order to evaluate the physical meaning of the differences between the values for $f_{S,P}$, $g_{S,P}$, and $h_{S,P}$ in Table 2, we proceeded to another fitting, wherein the parameters f_1, f_2, g_1, g_2, and h_1 were free to vary but constrained to having the same magnitude for all the curves. The obtained fits are presented in Fig. 3(b), where $f_1 = -0.087$, $f_2 = -0.21$, $g_1 = 2.74, g_2 = 1.31$, and $h_1 = 5.32$ for all plots. From the quality of these fits, we can establish that the small numerical differences in Table 2 are not physically significant and that the same set of tensor elements fits very well the experimental data.

While this formalism was first developed in view of the study of chiral molecules and structures, it is not restricted to their properties. For instance, it can also

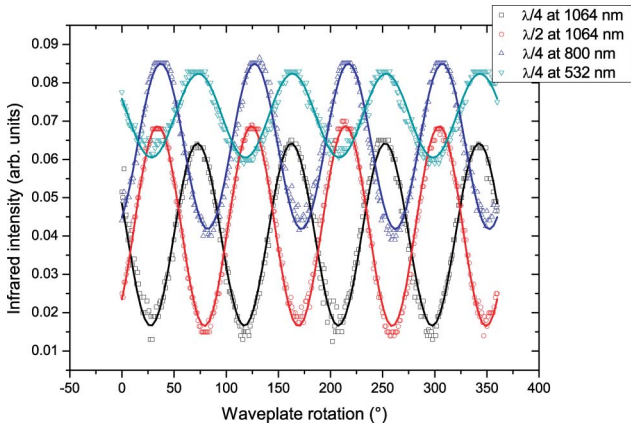

Fig. 3. (Color online) Intensity of the normalized second harmonic signal versus the angle of rotation of four different wave plates. The experimental data are indicated with open symbols, and the lines correspond to theoretical fits.

be applied in the investigations of anisotropic achiral materials such as an oxidized Si (001) at room temperature [10]. Indeed, in their recent publication, Li *et al.* reported that, generally speaking, if a phase shift is present between the bulk electric quadrupole and the surface dipole contributions to the SHG signal, a circular dichroism effect could be observed in the second harmonic. The circular dichroism magnitude can be expressed in terms of the coefficients $f_{S,P}$, $g_{S,P}$, and $h_{S,P}$. Since the authors attribute the presence of the bulk anisotropic contribution to a resonance at ~3.3 eV, we believe that an interesting next step in this type of study would be to investigate the effect at different wavelengths.

Therefore our experiment is important, not only for the spectroscopic study of chiral molecules and structures, but also in the case of anisotropic achiral materials.

5. Conclusions

In conclusion, we provided experimental evidence for a previously reported formalism, which allows the extraction of the $f_{S,P}$, $g_{S,P}$, and $h_{S,P}$ parameters from data recorded with a wave plate of any retardation (other than half-wave plate). More specifically, we measured the SHG response of a thin film consisting of chiral molecules, with four wave plates having distinctive retardation coefficients. By means of

Table 2. Fitting Parameters from the Fits in Fig. 3

	$\lambda/4$ at 1064 nm	$\lambda/2$ at 1064 nm	$\lambda/4$ at 800 nm	$\lambda/4$ at 532 nm
δ	2.07	−2.11	−1.57	1.08
θ_0	−17.5°	34°	37°	−16°
f_1	-0.283 ± 0.025	-0.243 ± 0.027	-0.141 ± 0.014	-0.121 ± 0.02
f_2	-0.115 ± 0.016	-0.154 ± 0.015	-0.248 ± 0.013	-0.193 ± 0.02
g_1	2.591 ± 0.027	2.655 ± 0.025	2.300 ± 0.064	2.002 ± 0.28
g_2	1.381 ± 0.015	1.315 ± 0.014	1.264 ± 0.021	1.235 ± 0.074
h_1	5.313 ± 0.018	5.353 ± 0.017	5.443 ± 0.019	5.427 ± 0.034
A	0.7	0.735	0.765	0.61

the fitting procedure described in the above-mentioned formalism, we demonstrated that a single set of tensor components fits all the data. This method can find applications in the studies of chiral structures and achiral anisotropic materials.

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