

Optical Second Harmonic Generation Chiral Spectroscopy

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An object or, more generally, a system of objects is called "chiral" if it differs from its mirror image in a way that the mirror image cannot be superimposed on the original. The two geometrical structures are then designated as "enantiomorphs". A great number of life-related molecules exhibit chirality and, therefore, experimental probes capable of distinguishing between enantiomorphs are highly desired in the fields of chemistry, biology, pharmacology and medicine.

Two of the most widespread chiro-optical spectroscopic techniques are circular dichroism (CD), which is based on the difference in absorption between left- and right-handed circularly polarized light, and optical rotatory dispersion (ORD), where the polarization of light is rotated to a different extent as function of the wavelength. As a well established scientific tool, CD can be used to help determine the structure of macromolecules (including the secondary structure of proteins and the handedness of DNA).^[1] Both CD and ORD are important tools for the study of biomolecules, their helical content and helix-coil transition.^[2] Nevertheless, these techniques are unable to detect reliably the chirality of a molecular monolayer of molecules, which limits greatly their use in situ, for instance, within biological systems.^[3]

It has been demonstrated that, on surfaces and interfaces the nonlinear optical techniques of second harmonic generation–circular dichroism (SHG–CD)^[4,5] and second harmonic generation–optical rotatory dispersion (SHG–ORD)^[6] are capable of distinguishing between left or right handed molecules, with a sensitivity that is much greater than that of their linear counterparts.

However, at the present moment, only a few SHG–CD and SHG–ORD spectra have been reported in the literature;^[7–9] other efforts for the development of a nonlinear optical chiral spectroscopic technique are concentrated on the dispersion of the second order susceptibility components.^[10] To our best knowledge a complete chiral spectroscopic study, combining all these aspects of the technique and demonstrating their interrelation is still lacking.

Here, we present an investigation of the dispersion of the nonlinear optical susceptibility tensor components, together with the SHG–CD and the SHG–ORD spectra, from a solid molecular film composed of chiral helicene molecules (Figure 1).

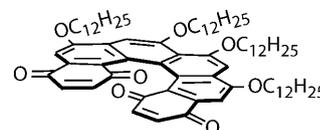


Figure 1. Structure of the sample molecule.

Our results are successfully fitted with the Lorenz model of the susceptibility and the consequential calculations are in very good agreement with the experimental observations. Based on its unprecedentedly large scope, we believe that our study constitutes a significant experimental step in the direction of establishing the SHG chiral spectroscopic technique.

The second-harmonic response can be described by a nonlinear polarization, which is expressed in the electric-dipole approximation by Equation (1).^[11]

$$P_{NL}(2\omega) = \chi^{(2)} \mathbf{E}(\omega) \mathbf{E}(\omega), \quad (1)$$

where ω is the frequency of light, $\chi^{(2)}$ is the second order susceptibility tensor and $\mathbf{E}(\omega)$ the electric field component of the incident light. It follows, from this formula, that SHG can only be generated in noncentrosymmetric materials or regions of matter that lack inversion symmetry, such as surfaces and interfaces. $\chi^{(2)}$ is a third rank tensor with 27 components, nevertheless, depending on the symmetry of the material, the number of nonvanishing susceptibility components can be significantly reduced. For an in-plane isotropic chiral sample (C_{∞} symmetry) the second order susceptibility is represented by Equation (2):

$$\chi^{(2)} = \begin{pmatrix} 0 & 0 & 0 & \chi_{xyz} & \chi_{xxz} & 0 \\ 0 & 0 & 0 & \chi_{yyz} & \chi_{yyz} & 0 \\ \chi_{zxx} & \chi_{zxy} & \chi_{zzz} & 0 & 0 & 0 \end{pmatrix}, \quad (2)$$

where $\chi_{xxz} = \chi_{yzz}$, $\chi_{xxz} = \chi_{yyz}$ and $\chi_{xyz} = \chi_{yxz}$. This last component leads to the appearance of nonlinear optical activity (the nonlinear equivalent of optical activity) and henceforth is responsible for the SHG–CD and SHG–ORD effects. Often this component is referred to as the chiral one, since it is present only in chiral systems. The other components are referred to as achiral because they occur in both chiral and achiral systems.

Within the Lorentz model of the susceptibility, we can express $\chi^{(2)}$ in terms of the resonance frequency ω_0 as shown in Equation (3).^[10]

$$\chi^{(2)}(2\omega) = \xi^{(2)} \frac{Ne^2}{m^2} \frac{1}{(\omega_0^2 - 4i\gamma\omega - 4\omega^2)} \times \frac{1}{(\omega_0^2 - 2i\gamma\omega - \omega^2)^2} \quad (3)$$

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where $\xi^{(2)}$ is the first anharmonic term that characterizes the strength of the nonlinearity, N is the electronic number density, e and m are the charge and the mass of the electron, and γ is the damping constant.

It has been shown that the second-harmonic field can be conveniently written in terms of the s - and p -polarized components of the fundamental field [Eq. (4)].^[12]

$$\mathbf{E}(2\omega) = f\mathbf{E}_p^2(\omega) + g\mathbf{E}_s^2(\omega) + h\mathbf{E}_p(\omega)\mathbf{E}_s(\omega), \quad (4)$$

where f , g and h are complex numbers, which are linear combinations of the Cartesian susceptibility tensor components $\chi_{ijk}^{(2)}$. In the following, we shall indicate the real and imaginary part of these complex values by the indices 1 and 2, respectively. The three coefficients in Equation (4) also include the nonlinear Fresnel factors. Furthermore, just as the nonlinear susceptibility, the exact form of these three parameters depends on the symmetry of the sample. In addition, their value can be affected by the angle of optical incidence, the experimental geometry and is different for the S - and P -polarized component of the SH-field. Neglecting the refractive indices, for a chiral isotropic surface in the electric dipole approximation and in the transmission geometry, the dependence of f , g and h on the different susceptibility components takes the form of Equation (5).^[13]

$$\begin{aligned} f_s &= \sin\theta(2\chi_{xyz}\cos\theta) \\ g_s &= 0 \\ h_s &= \sin\theta(2\chi_{xxz}) \\ f_p &= \sin\theta(2\chi_{zzz}\sin^2\theta + \chi_{zzx}\cos^2\theta + 2\chi_{xxz}\cos^2\theta) \\ g_p &= \sin\theta(\chi_{zxx}) \\ h_s &= -\sin\theta(2\chi_{xyz}\cos\theta) \end{aligned} \quad (5)$$

where the subscripts S and P refer to the particular component of the SH-field.

The SHG-CD is then defined as the difference between the SHG intensity for left and right incoming circularly polarized light, divided by half the sum. This quantity can be expressed in terms of the complex parameters f , g and h as shown in Equation (6):

$$\begin{aligned} I_{\text{SHG-CD}} &= \frac{I_{\text{LCP}}(2\omega) - I_{\text{RCP}}(2\omega)}{\frac{1}{2}(I_{\text{LCP}}(2\omega) + I_{\text{RCP}}(2\omega))} \\ &= \frac{4[(f_2 - g_2)h_1 - (f_1 - g_1)h_2]}{|f|^2 + |g|^2 + |h|^2 - 2(f_1g_1 + f_2g_2)} \end{aligned} \quad (6)$$

It is apparent from this equation that SHG-CD is due to an interference between the achiral and the chiral susceptibility components.

For P -polarized input, and choosing $\theta = 45^\circ$, the SHG optical rotation can be expressed as Equation (7):^[13]

$$|\phi| = \tan^{-1}\left(\frac{|f_s|}{|f_p|}\right) = \tan^{-1}\left(\frac{|h_p|}{|f_p|}\right) \quad (7)$$

Figure 2 shows the SHG intensity as function of incoming fundamental wavelength for three of the four main linear polarization combinations, namely $P_{\text{IN}}-S_{\text{OUT}}$, $S_{\text{IN}}-P_{\text{OUT}}$ and $P_{\text{IN}}-P_{\text{OUT}}$.

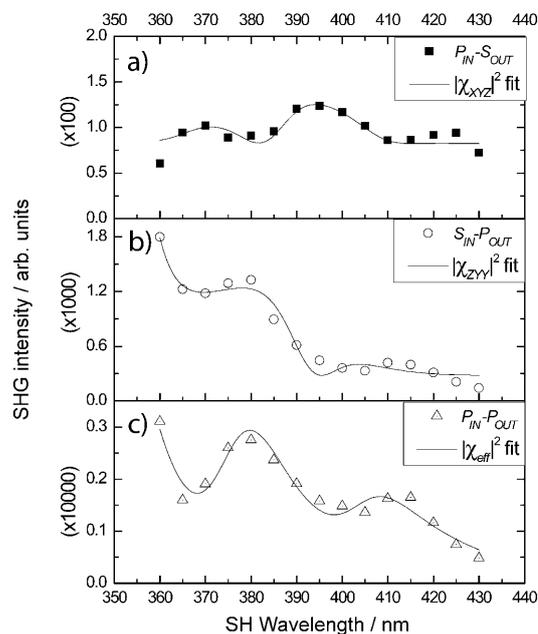


Figure 2. The symbols indicate the experimentally recorded SHG intensity as function of the second harmonic wavelength for three linear polarization combinations. The lines constitute fits with the Lorentz model of the susceptibility.

As it can be seen from Equation (2), these particular combinations address specific tensor components of the nonlinear susceptibility. Especially, in the $P_{\text{IN}}-S_{\text{OUT}}$ configuration (Figure 2a), the SHG signal is proportional to the chiral χ_{xyz} component, while in the $S_{\text{IN}}-P_{\text{OUT}}$ and $P_{\text{IN}}-P_{\text{OUT}}$ settings (Figures 2b and c) it is the achiral tensor elements that contribute. Consequently, the data were fitted with Equation (3) using arbitrary units for the constant terms on the right hand side of the equation. We found that the minimum number of resonances which allows us to fit the data was three, however these fits were not unique.

The fits in Figure 2 correspond to the square of the norm of the nonlinear susceptibilities. After extracting the real and imaginary parts, we obtained the complex parameters f , g and h from Equation (5). Further establishing the validity of this procedure, for each parameter, it was verified that the real and imaginary parts are Kramers-Kronig transforms of each other. Calculating the SHG-CD and SHG-ORD response using Equations (6) and (7) respectively was then straightforward.

At this stage we fitted simultaneously all the graphs in Figure 2, together with the measured SHG-CD and the SHG-ORD. Figure 3a presents the measured SHG-CD response of the sample as function of the wavelength, as well as the calculated SHG-CD values. A clear agreement between the two can be observed and therefore we can attribute the variations of the SHG-CD spectrum to the resonances in the chiral and achiral parts of the nonlinear susceptibility, namely: 384 (2), 365 (5)

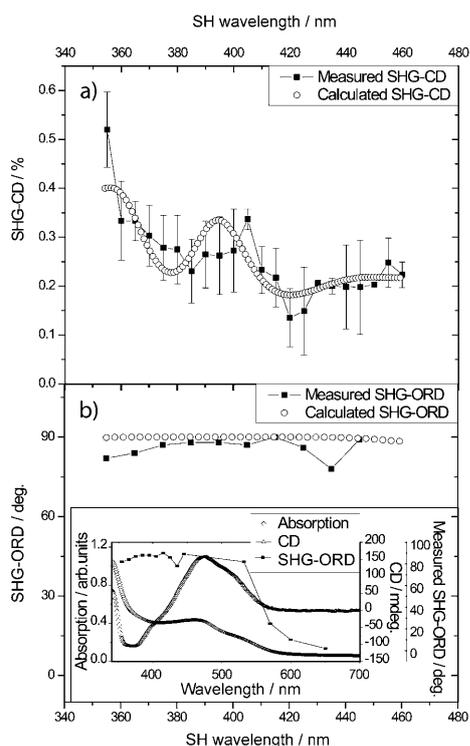


Figure 3. The measured and calculated SHG-CD (a) and SHG-ORD (b) response of the sample as function of the second harmonic wavelength. Inset in (b), the linear CD, the absorption and the SHG-ORD spectra as function of the second harmonic wavelength.

and 409 (3) nm for Figure 2a, 321 (49), 356 (2) and 394 (8) nm for Figure 2b, and 341 (88), 374 (3) and 403 (6) nm for Figure 2c, where the numbers within brackets are the fitting uncertainties. Within the combined uncertainty of the experiments and the fits, and having in mind that the FWHM value of the femtosecond pulses extends over 15 nm, it can be said that the three resonances in Figure 2 are the same. To our best knowledge, this is the first result that shows that the SHG-CD spectrum can be related to the material resonances, although clearly this relationship is not a simple one.

Figure 3b shows the measured SHG-ORD spectrum as function of the wavelength, as well as the calculated response. As can be seen in the inset of that figure, experimentally, it is observed that with decreasing wavelength, upon resonance, the nonlinear optical rotation increases to the point of saturation at 90° . This can be understood from Equation (6), where, having in mind Equation (5), we see a ratio between the norms of the chiral (Figure 2a) and the achiral (Figure 2c) tensor components. In Figure 2, it can be seen that the values of the former are two orders of magnitude larger than those of the latter. Consequently, the ratio of these quantities is very large and, upon taking the inverse tangent, saturation is reached. For comparison, the linear CD and ORD spectrum of the molecules is also given in the inset. As it can be seen, the units there are only millidegrees. Furthermore, there is no obvious correlation between the nonlinear and linear CD/ORD spectra. For example, in the linear case, there is a clear change in the sign of the CD response which can be related to the structural

properties of the sample. No such sign reversal can be observed in the SHG-CD, from this particular sample. However, overall sign reversal does play a crucial role in SHG-CD, since it allows distinguishing between different enantiomorphs.

While in linear optics, CD and ORD spectra are redundant through the Kramers–Kronig relations, and therefore one is sufficient, in the nonlinear case, we believe that the presence of a large number of fitting parameters requires several experiments in order to introduce additional constraints to the fittings.

In conclusion, we investigated the dispersion of the nonlinear optical susceptibility tensor components and the SHG-CD and SHG-ORD spectra from a solid molecular film composed of chiral helicenebisquinone molecules. While the first measurement provides information on the molecular properties of the sample, the second and third ones probe specifically the chirality. Verifying the interrelation between molecular resonances and chirality in SHG studies, our data were fitted with the Lorenz model of the susceptibility and the ensuing calculations were found to be in very good agreement with the experimental results. Therefore, our findings constitute an important experimental milestone towards the development of a SHG chiral spectroscopic technique and open up new possibilities for studying the three-dimensional structure of chiral molecules, such as proteins.

Experimental Section

The experiments were performed with a tunable Ti:Sapphire laser system, many of the principle features of which were described extensively elsewhere.^[14] The polarization of the electromagnetic radiation was manipulated by, either a half wave-plate or a Berek Polarization Compensator set on different retardations throughout the experiment. The angle of optical incidence θ was 45° on the specimen. Part of the beam was directed towards a photodiode, which was connected to the analog voltage input of a lock-in amplifier, 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 by means of an optical chopper. The spectroscopic results presented here were calibrated using a quartz crystal. All the fits were performed in Origin.

The sample was a Langmuir-Blodgett thin film (γ -deposition, 300 layers) of an enantiomerically pure chiral helicenebisquinone,^[15,16] deposited on a glass substrate.

UV/Vis absorption spectra were recorded with a Perkin-Elmer Lambda 900 Spectrometer and the linear CD-measurements were performed on a Jasco J-810 Spectropolarimeter.

Acknowledgements

We acknowledge financial support from the Fund for scientific research Flanders (FWO-V) and the University of Leuven (GOA). S.F. acknowledges financial support from the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT—Vlaanderen). We also would like to thank Prof. T. J. Katz for providing the helicene as well as Rik Strobbé and Frans Hennau for their technical support.

Keywords: chirality · circular dichroism · nonlinear optics · second harmonic generation · ultrafast spectroscopy

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Received: January 21, 2009

Published online on March 12, 2009