LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1995 issue.

COMMUNICATIONS

Linearly polarized probes of surface chirality

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We present a new nonlinear optical technique to study surface chirality. We demonstrate experimentally that the efficiency of second-harmonic generation from isotropic chiral surfaces is different for excitation with fundamental light that is +45° and −45° linearly polarized with respect to the *p*-polarized direction. © *1995 American Institute of Physics.*

In linear optics, chiral molecules are known for their ability to rotate the plane of polarization of linearly polarized light that propagates through a sample of the chiral material. Other examples of such linear optical-activity effects are circular dichroism and optical rotatory dispersion.[1] All these effects arise from the different response of chiral molecules to left- and right-hand circularly polarized light. In isotropic solutions of chiral molecules, such circular-difference effects arise from contributions of magnetic-dipole transitions to the linear optical properties of chiral media.

Optical-activity effects have been predicted to occur also in nonlinear optics[2–4] and several examples of nonlinear optical activity have recently been observed experimentally. Nonlinear optical activity was first observed in second-harmonic generation (SHG) from chiral binaphtol molecules adsorbed at an air–water interface[5] and subsequently from thin films of helical polyisocyanides[6] and bacteriorhodopsin.[7] In these experiments, circularly polarized incident light was used to excite the chiral surface and the efficiency of SHG was found to be different for the two circular input polarizations. Rotation of the dominant polarization component of the second-harmonic light emanating from a chiral surface with respect to a linear input polarization has also been observed.[8] We have also developed a general theory of SHG from chiral surfaces that includes contributions of electric- and magnetic-dipole transitions to the surface nonlinearity.[9] This theory has been successfully used to describe the experimentally observed circular-difference effects in SHG from chiral surfaces.

In this Communication we show that, in addition to circular polarizations, appropriately chosen linear polarizations of the fundamental light can also be used to probe the chiral properties of isotropic surfaces. We demonstrate that excitation of a chiral surface with fundamental light polarized at either +45° or −45° with respect to the *p*-polarized direction gives rise to a difference in the intensity of the second-harmonic light emanating from the surface. To the best of our knowledge, this "linear-difference" effect has never been observed experimentally. However, analogous effects have been predicted to occur in Raman optical activity, although these experiments have not been attempted.[10] We also note that recently a very general formalism describing second-order nonlinear light scattering, including possible linear- and circular-difference effects, has been developed.[11,12]

The intensity of the second-harmonic light generated by a surface can always be expressed in the general form:[9]

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

where $E_p(\omega)$ and $E_s(\omega)$ refer to the *p*- (parallel to the plane of incidence) and *s*-polarized (perpendicular to the plane of incidence) components of the fundamental field, respectively. The coefficients f, g, and h are linear combinations of different electric-dipole and magnetic-dipole susceptibility components and the relative weights of these combinations are different for the reflected and transmitted *s*- and *p*-polarized components of the second-harmonic field.[9]

For the case of linearly polarized incident light that is rotated by ±45° from the *p*- (or *s*-) polarized direction, $E_p=\pm E_s$. Hence, the intensity of the second-harmonic field for +45° or −45° excitation is

$$I(2\omega)=|f+g\pm h|^2I^2(\omega). \qquad (2)$$

From Eq. (2) it is clear that difference effects for ±45° linear excitation (linear-difference effects) arise from the in-phase components of the coefficients $(f+g)$ and h, i.e., from the real (imaginary) part of h combined with the real (imaginary)

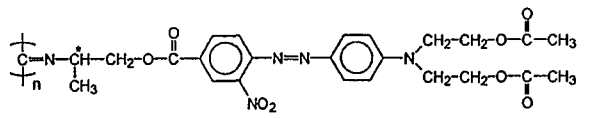

FIG. 1. Chemical structure of the S-enantiomer of the chromophore functionalized poly(isocyanide).

part of $(f+g)$. For off-resonant exitation, $(f+g)$ and h are real quantities and, to the first approximation, functions of the electric-dipole allowed susceptibility components of the chiral surface. For near-resonant excitation the situation is more complicated since f, g, and h become complex quantities. Furthermore, the importance of the magnetic-dipole nonlinearity is enhanced under resonant excitation. It is also important to note that depending on the second-harmonic signal measured, the combination $(f+g)$ or h is vanishing for achiral surfaces.[9] Therefore, a linear-difference effect can occur only for chiral surfaces. Note also that the circular-difference effects in SHG (i.e., different responses of SHG to left-hand and right-hand circularly polarized fundamental light) can occur only when a phase-difference exists between the coefficient h and the other two coefficients (f and g).

Linear-difference effects were studied experimentally in Langmuir–Blodgett films of the S-enantiomer of a chiral polymer [a poly(isocyanide) functionalized with a nonlinear optical chromophore, Fig. 1] mixed with poly(-S-1-acetoxymethylethylisocyanide). These polyisocyanides form rigid-rod helices on a water surface and can be easily transferred to a solid substrate by means of the Langmuir–Blodgett method.[13] The sample used consists of 18 layers of z-type deposited films and is slightly absorbing at the second-harmonic frequency. The fundamental beam of a Q-switched and injection-seeded Nd:YAG laser (1064 nm, 10 ns pulses, 50 Hz) is used to pump the sample at the angle of incidence of 45°. The polarization of the fundamental beam is continuously varied by rotating a half-wave plate and the intensity of the second-harmonic (p- or s-polarized) light is recorded in reflection and transmission. Sufficient polarization purity of the experiment was verified by making sure that no linear-difference effects were observed in the second-harmonic intensity generated from achiral samples.

The observed SHG is attributed to the chromophore functionalized polyisocyanide and significant linear-difference effects are observed in the SHG emanating from the Langmuir–Blodgett samples. The results for the p- and s-polarized transmitted and reflected signals are shown in Figs. 2(a), 2(b), 3(a), and 3(b), respectively. The linear-difference effects can be quantified in terms of the ratio of the difference of intensities of the detected second-harmonic light for ±45° linearly polarized exitation and the average intensity as $\Delta I/I = 2(I_{-45°} - I_{+45°})/(I_{-45°} + I_{+45°})$. For the results of Figs. 2(a), 2(b), 3(a), and 3(b), the values of the linear-difference effect are 47%, 56%, 51%, and 36%, respectively. These values are of the same order of magnitude as those observed for circular-difference effects in SHG from

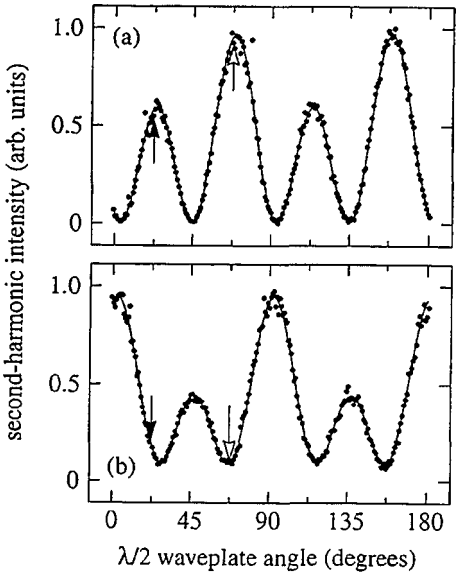

FIG. 2. Reflected second-harmonic signal versus the rotation angle of the half-wave plate for (a) the s-polarized component and (b) the p-polarized component. The black and white arrows indicate the +45° and −45° linear polarizations, respectively. The solid lines are a guide to the eye.

chiral surfaces, and orders of magnitude higher than those observed for linear circular dichroism.

The magnitude of the linear-difference effects suggests that this novel nonlinear optical activity technique can be used as a simple and attractive method to study weakly chiral samples. Combined with the surface-specifity of second-harmonic generation, we also believe that this technique can be a powerful method to investigate the chiral properties of

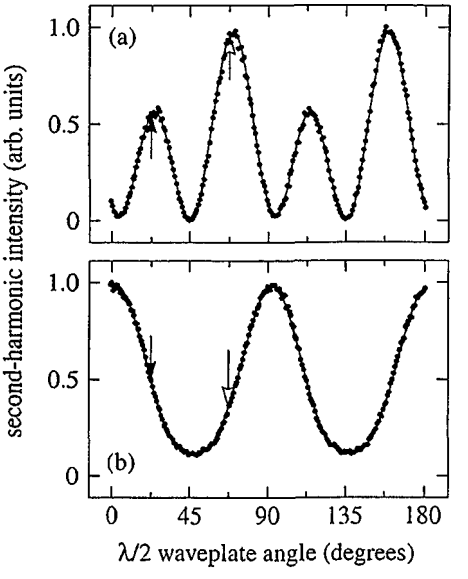

FIG. 3. Transmitted second-harmonic signal versus the rotation angle of the half-wave plate for (a) the s-polarized component and (b) the p-polarized component. The black and white arrows indicate the +45° and −45° linear polarizations, respectively. The solid lines are a guide to the eye.

surfaces and membranes without the need to use circular polarizations. In addition, the fact that linear-difference effects do not require a phase-difference between the coefficients $(f+g)$ and h (i.e., the components of the susceptibility tensor) to occur implies that these effects can also be observed under nonresonant excitation. Hence, the linear-difference effects can be used as a complementary tool to the circular-difference effects, which are expected to disappear under nonresonant conditions. A significant advantage of working under nonresonant conditions is the reduction in the risk of laser damage to the sample under study. We also believe that the linear-difference effect is advantageous compared to the SHG analog of optical rotatory dispersion,[8] which can also be used to probe surface chirality under nonresonant conditions. In the linear-difference technique, the input and output polarizations are prescribed while in the SHG optical rotatory dispersion technique a search procedure for the largest polarization component of the SHG field is necessary. Finally, it is also interesting to note that the linear-difference effect has no analogue in linear optical activity of bulk samples. The difference between the linear optical technique and our nonlinear optical technique is related to the type of sample. In the case of the nonlinear technique, the surface breaks the symmetry between the s- and p-polarized directions. On the other hand, for the case of bulk samples, the expansion of the input field in terms of s- and p-polarized components is meaningless.

In conclusion, we have demonstrated that the efficiency of SHG from chiral isotropic surfaces is different for fundamental light that is $+45°$ and $-45°$ polarized with respect to the p-polarized direction. This linear-difference effect has not been experimentally observed before and is expected to play an important role in the study of chirality.

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