Optical Activity of Anisotropic Achiral Surfaces

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Anisotropic achiral surfaces respond differently to left- and right-hand circularly polarized light. This occurs when the orientation of the surface with respect to an otherwise achiral experimental setup makes the total geometry chiral. Such optical activity is demonstrated in second-harmonic generation from an anisotropic thin molecular film. The circular-difference response reverses sign as the handedness of the geometry is reversed and vanishes when the setup possesses a mirror plane. The results are explained within the electric-dipole-allowed second-order surface nonlinearity. [S0031-9007(96)00778-8]

PACS numbers: 33.55.Ad, 42.65.Ky, 78.66.–w

Optical-activity effects, e.g., circular dichroism and optical rotation, are usually associated with chiral (enantiomorphous) materials [1]. Such materials possess no mirror planes and occur in two enantiomers that are mirror images of each other. Optical activity arises from the different interaction of chiral materials with left- and right-hand circularly polarized light and reverses sign between the enantiomers. For isotropic chiral solutions, optical activity arises from the interference between the electric-dipole and magnetic-dipole contributions to the optical properties of the material [1]. However, for surface geometries with only two-dimensional rotational symmetry, chiral effects can also be allowed in the electric-dipole approximation [2].

On a more general level, the term optical activity is used to refer to circular-difference and optical-rotation effects that occur beyond (linear) birefringence. Such effects can occur also in achiral materials. This is possible if the experimental arrangement is chiral, i.e., it possesses a definite handedness and is described by three noncoplanar unit vectors [3]. For example, photoelectron emission from oriented linear molecules exhibits optical activity if the direction of propagation of the incident photon and the photoelectron and the axis of the molecule are not coplanar [3]. In addition, optical rotation can occur in certain nonenantiomorphous crystals [4] and oriented molecular systems [5] such as nematic liquid crystals [6,7]. However, these cases involve light propagation in a bulk sample and, consequently, separation between optical activity and linear birefringence may be very difficult [8]. Optical activity has also been observed in second-harmonic generation from an isotropic and achiral surface [9]. In this case the chirality of the experiment was not associated with the orientation of the sample but arose from the (mis)alignment of the polarizer that was used to analyze the second-harmonic light.

In this Letter, we report the first observation of optical activity of achiral anisotropic surfaces. We use the all-optical technique of surface second-harmonic generation

[10], which simplifies the experiment considerably compared to photoelectron emission experiments. Second-harmonic generation has already been shown to be a sensitive probe of chiral isotropic surfaces [11]. Our surface consists of a thin film of oriented molecules. The interpretation of the results is straightforward since the second-harmonic response originates only from the molecular layer and effects due to propagation and linear birefringence are negligible. Furthermore, unlike photoelectron emission from single molecules, second-harmonic generation is a coherent process. Hence, although the structure of our molecules is essentially linear, two unit vectors, the surface normal and the in-plane symmetry axis, are necessary to specify the orientation of the sample with respect to the photon propagation direction, which provides the third unit vector. The experiment can therefore be performed in a collinear transmission geometry. The simplicity of the experiment allows us to perform an extensive study of this second-order optical activity under reflection operations that reverse the handedness of the setup. The results are explained by an electric-dipole-allowed second-order surface nonlinearity.

In our experiments, we used Langmuir-Blodgett (LB) films of 2-docosylamino-5-nitropyridine (DCANP) [12] as the anisotropic achiral sample. The LB films used in the experiment consisted of 10 molecular layers with a total thickness of $\sim$22 nm. The films belong to the achiral C_{1h} symmetry group where the molecules are preferentially aligned along the in-plane symmetry axis. To specify the experimental geometry, we take the x and z axes along the anisotropy axis and the surface normal, respectively (Fig. 1). The direction of propagation of the fundamental beam with respect to the sample is characterized by the angle of incidence θ and the in-plane (azimuthal) rotation angle ϕ. Note that for the angles $\phi = 0°$ or $\phi = 180°$ and $\theta = 0°$ or $180°$, the plane of incidence is a mirror plane and the setup is achiral. For any other values of these angles, the setup is chiral with a definite handedness. The handedness can be reversed by
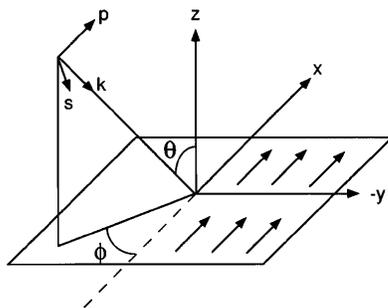
FIG. 1. Experimental geometry: fundamental laser beam (wave vector k, s- and p-polarized field components) is incident on the sample at an angle θ. The azimuthal rotation of the sample is characterized by ϕ. The arrows on the sample indicate the alignment of DCANP molecules along the dipping direction that creates the anisotropy axis. The anisotropy axis and the surface normal are along the x and z directions, respectively.

FIG. 2. Experimental geometry for azimuthal angles of $\phi = 0°$, $-90°$, and $+90°$. k_ω is the wave vector of the fundamental beam and $k_{2\omega}$ the wave vector of the transmitted second-harmonic beam.

two different reflection operations, one characterized by

$$\theta \to \theta, \qquad \phi \to -\phi, \tag{1}$$

and the other by

$$\theta \to -\theta, \qquad \phi \to 180° - \phi. \tag{2}$$

In our experiments, the fundamental beam of a Q-switched Nd:YAG laser $(1064\text{ nm}, 50\text{ Hz}, \sim 10\text{ ns})$ is used to pump the sample at incidence angles of $\pm 43°$ or $\pm 37°$. The sample is mounted on a rotation stage that allows for rotation around the surface normal (z axis). The intensity of the second-harmonic light emanating from the sample is measured for left- and right-hand circularly polarized fundamental excitation. The second-harmonic intensity is detected by a photomultiplier and separated from the fundamental light by means of an IR blocking filter and a 532 nm interference filter. Circular-difference effects are expressed in terms of the sum and difference of the intensities of the detected second-harmonic light for left- and right-hand circularly polarized excitation as $\Delta I/I = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$. Sufficient polarization purity of the experiment is verified by making sure that no circular-difference effects are observed in the second-harmonic intensity generated from achiral isotropic samples. To demonstrate the optical activity of our anisotropic surface, it is advantageous to consider the p-polarized transmitted second-harmonic signal and azimuthal rotation angles $\phi = 0°$ and $\phi = \pm 90°$ (Fig. 2).

The experimental results for all combinations of the angles θ and ϕ are summarized in Table I. Circular-difference effects were never observed for sample orientations $\phi = 0°$ or $\phi = 180°$. In these cases, the anisotropy axis of the sample is in the plane of incidence, which is a mirror plane of the experimental configuration including the sample. On the other hand, substantial circular-difference effects were observed for sample orientations of $\phi = \pm 90°$ and the difference effects change sign be-
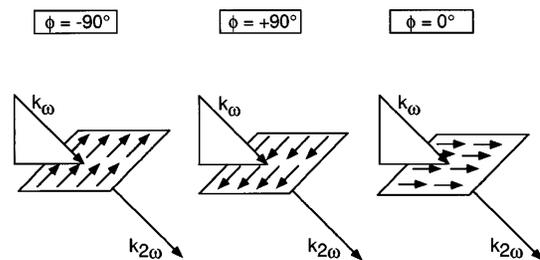
tween these two orientations. The magnitude of the difference effects remains unchanged. Furthermore, the difference effects also change sign between the positive and negative angles of incidence θ. These results show that the circular-difference response reverses sign as the handedness of the sample orientation is reversed, i.e., as one of the angles θ and ϕ changes sign. So, by changing the angle of incidence or the orientation of the sample it is possible to create different enantiomers of the experimental configuration. It is important to note that the experimental setup without the sample is achiral. Hence, optical activity effects from isotropic thin films cannot be observed. On the other hand, addition of an anisotropic film breaks the symmetry of the experimental geometry for certain orientations of the film and gives rise to optical activity effects.

To explain the observed effects theoretically, we consider second-harmonic generation from an anisotropic surface. The second-harmonic intensity generated from a surface or thin film is of the form [13]

$$I(2\omega) = | fE_p(\omega)E_p(\omega) + gE_s(\omega)E_s(\omega)$$
$$+ hE_s(\omega)E_p(\omega)|^2, \tag{3}$$

where $E_p(\omega)$ and $E_s(\omega)$ are the p- and s-polarized components of the fundamental field incident on the

TABLE I. Experimentally observed circular-difference effects $\Delta I/I = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$ for different sample orientations ϕ and angles of incidence θ. The intensity of the p-polarized second-harmonic field in transmission was detected.

Incidence angle θ	Sample orientation ϕ	Circular-difference effect
$+43°$	$0°, 180°$	$(0 \pm 2)\%$
	$-90°$	$-(6 \pm 1)\%$
	$+90°$	$+(7 \pm 1)\%$
$-43°$	$0°, 180°$	$+(1 \pm 2)\%$
	$-90°$	$+(7 \pm 1)\%$
	$+90°$	$-(8 \pm 1)\%$

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surface. The coefficients f, g, and h are linear combinations of the various second-order (surface) susceptibility components, and they are unique to any detected second-harmonic signal. For circularly polarized excitation, $E_p(\omega) = \pm iE_s(\omega)is$ and

$$I(2\omega) = |-f + g \pm ih|^2 I^2(\omega), \qquad (4)$$

where the upper and lower signs correspond, respectively, to right- and left-hand circular polarizations and $I(2\omega) = |E_s(\omega)|^2$. From Eq. (4) it is clear that circular-difference effects in second-harmonic generation can occur if $-f + g$ and h are simultaneously nonvanishing. For the case of isotropic surfaces, this is only possible if the surface is also chiral. However, as we will show in detail, for the case of anisotropic surfaces chirality is not required. Note also that circular-difference effects can only occur when, at least, a portion of the coefficient h is out of phase with one of the other two coefficients.

For an anisotropic sample such as our DCANP film, the expansion coefficients f, g, and h depend on the orientation of the sample in the setup. It can be shown in general that, depending on the second-harmonic signal, either $-f + g$ or h but not both reverses sign under the operations specified by Eqs. (1) and (2). Hence, the circular-difference effects are expected to reverse sign as the handedness of the setup changed. We next specialize to the particular configurations studied in the experiment. For the rotation angle $\phi = 0°$ we find

$$f = \chi_{zzz} \sin^3\theta + \chi_{xxx} \cos^3\theta + [\chi_{xzz} + 2\chi_{zzx}]$$
$$\times \sin^2\theta \cos\theta + [\chi_{zxx} + 2\chi_{xxz}] \sin\theta \cos^2\theta,$$

$$g = \chi_{xyy} \cos\theta + \chi_{zyy} \sin\theta,$$

$$h = 0,$$

where χ_{ijk} are the components of the electric-dipole-allowed second-order susceptibility tensor and the Fresnel factors at the fundamental and second-harmonic frequencies have been absorbed in the tensor components. For this achiral orientation, the plane of incidence is a mirror plane and the coefficient h vanishes. Consequently, circular-difference effects cannot occur. For the chiral sample orientations, the coefficients are

$$f = \chi_{zzz} \sin^3\theta + [\chi_{zyy} + 2\chi_{yyz}] \cos^2\theta \sin\theta,$$

$$g = \chi_{zxx} \sin\theta,$$

$$h = \pm(2\chi_{zzx} \sin^2\theta + 2\chi_{yyx} \cos^2\theta),$$

where the $\pm$ sign in h refers to $\phi = \pm 90°$ of rotation. For these orientations, there are no mirror planes in the experimental geometry including the sample, and f, g, and h are simultaneously nonvanishing. Hence, optical activity effects can occur. Furthermore, the sign of these effects is reversed for the $+90°$ and $-90°$ orientations because h changes sign. In addition, changing the incidence angle from $+\theta$ to $-\theta$ also reverses the sign of the optical activity effects. Hence, as found experimentally, rotating the sample around the x or z axis creates different enantiomers of the experimental geometry.

For isotropic surfaces, the expansion coefficients f, g, and h are independent of the orientation of the sample in the setup. For isotropic achiral surfaces, the nonvanishing components of the electric-dipole-allowed second-order susceptibility are zzz, $zxx = zyy$, and $xxz = yyz$. Hence, h will always be zero for p-polarized second harmonic in transmission and optical activity effects cannot occur. On the other hand, for isotropic chiral surfaces an additional xyz component is present in h and optical activity effects can occur, independent of sample orientation.

Note that Eq. (3) implies that for the linear polarizations that are rotated by $\pm 45°$ from the p-polarized direction ($E_p = \pm E_s$), the intensity of the SHG field is

$$I(2\omega) = |f + g \pm h|^2 I^2(\omega). \qquad (5)$$

Hence, these two linear input polarizations can also be used as a probe of surface chirality [14]. We have also verified that these linear-difference effects can be used to probe the optical activity of our anisotropic surface (Table II). The results are analogous to those of the circular-difference effects. However, one can argue that the circular-difference response provides a more fundamental probe of optical activity of anisotropic surfaces than the linear-difference response. The two circular input polarizations are characterized by their helicity which is directed parallel or antiparallel to the photon propagation direction [7]. On the other hand, the linear input polarizations are characterized by additional vectors that can, in principle, influence the handedness of the experiment [7].

In principle, optical activity effects analogous to those described in this Letter should also occur in linear optical processes. However, experimental observation of these effects is more difficult because linear processes are not surface specific. Consequently, substrate interference is expected to mask any possible linear optical-activity effects.

In conclusion, we have shown that optical activity can be observed in second-harmonic generation from achiral anisotropic thin films. The effects reverse their sign

TABLE II. Experimentally observed linear-difference effects $\Delta I/I = 2(I_{-45°} - I_{+45°})/(I_{-45°} + I_{+45°})$ for different sample orientations ϕ and angles of incidence θ. The intensity of the p-polarized second-harmonic field in transmission was detected.

Incidence angle θ	Sample orientation ϕ	Linear-difference effect
$+37°$	$0°, 180°$	$(0 \pm 2)\%$
	$-90°$	$+(9 \pm 2)\%$
	$+90°$	$-(9 \pm 2)\%$
$-37°$	$0°, 180°$	$(0 \pm 2)\%$
	$-90°$	$-(9 \pm 3)\%$
	$+90°$	$+(11 \pm 2)\%$

as the handedness of the experiment is reversed. The observed effects can be described theoretically by the electric-dipole-allowed second-order surface nonlinearity. We expect that these effects can have important consequences in the study of complex chiral structures, since the presence of anisotropy can yield information that is not connected to the chirality of the system under investigation. On the other hand, we believe that the effects can be used to advantage in the characterization of anisotropic achiral surfaces.

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