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Chiral Molecules Split Light: Reflection and Refraction in a Chiral Liquid

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A light beam changes direction as it enters a liquid at an angle from another medium, such as air. Should the liquid contain molecules that lack mirror symmetry, then it has been predicted by Fresnel that the light beam will not only change direction, but will actually split into two separate beams with a small difference in the respective angles of refraction. Here we report the observation of this phenomenon. We also demonstrate that the angle of reflection does not equal the angle of incidence in a chiral medium. Unlike conventional optical rotation, which depends on the path-length through the sample, the reported reflection and refraction phenomena arise within a few wavelengths at the interface and thereby suggest a new approach to polarimetry that can be used in microfluidic volumes.

Liquids composed of randomly oriented molecules are, in the absence of an external influence, isotropic, and are generally described by a single scalar refractive index. Optically active liquids, that is, chiral liquids which have the ability to rotate the polarization vector of light, are an important exception. These are characterized by two refractive indices: one for left- $(-)$ and one for right- $(+)$ circularly polarized radiation. Linearly polarized light may be regarded as a coherent superposition of left- and right-circularly polarized waves of equal amplitude, and Fresnel's theory of optical rotation shows that a difference in the respective indices of refraction causes the waves to acquire different phases as they propagate through the liquid and the polarization vector to rotate [1,2]. The significance of optical rotation lies in the fact that it is a means to distinguish the two mirror image forms (enantiomers) of a chiral molecule. Most biologically important molecules are chiral and optical rotation is a well-established analytical technique used to determine their absolute stereochemical configuration (handedness) in solution. Optical activity in liquids should, however, not only manifest itself through optical rotation in transmission, but should also be observable in reflection and refraction [3–7], as we demonstrate in this Letter.

If one considers the refraction of light at a boundary formed by a chiral and an achiral isotropic medium, as shown in Fig. 1(a), then the circularly polarized components must independently obey Snell's law:

$$n_0 \sin\theta_0 = n^{(\pm)} \sin\theta^{(\pm)}. \qquad (1)$$

Circularly polarized light, incident with angle of incidence θ_0 from the achiral medium characterized by the polarization independent refractive index n_0, will thus refract with angles of refraction $\theta^{(-)}$ and $\theta^{(+)}$, depending on whether it is, respectively, left- or right-circularly polarized [1,3,4,8]. Similarly, if unpolarized or linearly polarized light is incident from the achiral medium, then the light will split into

two beams, one left- and the other right-circularly polarized [3,5].

In order to verify that a linearly polarized light beam does split into its left- and right-circularly polarized components as shown in Fig. 1(a), we imaged the separation between the two refracted beams on a CCD camera. Given that the difference between the refractive indices is small, the angular divergence $\delta = \theta^{(+)} - \theta^{(-)}$ between the refracted beams in Fig. 1(a) can be written as

$$\delta \approx \frac{\tan\theta}{n}(n^{(-)} - n^{(+)}), \qquad (2)$$

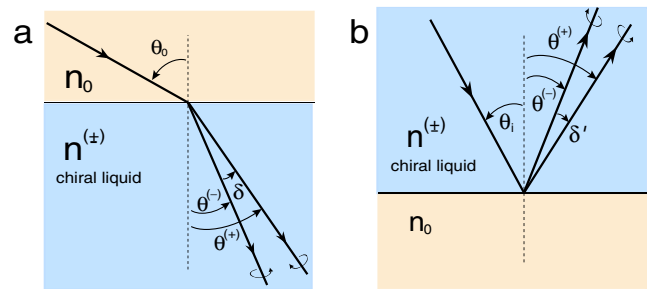where $n = (n^{(-)} + n^{(+)})/2$ and where θ is the average of

FIG. 1 (color online). (a) Refraction geometry at an achiral-chiral interface. A wave incident from an isotropic achiral medium (angle of incidence θ_0) is split into its circularly polarized wave components in the chiral medium. In an achiral medium the angle of reflection (not shown) does not depend on the polarization of the light and is therefore not sensitive to chirality. However, Silverman *et al.* showed that the specular reflection off a chiral surface can exhibit differences in intensity for the two circularly polarized components that depend on the circular dichroism (differential absorption) in the chiral medium [19]. (b) Reflection geometry at a chiral-achiral interface *in a* chiral medium. A wave incident from a chiral medium is reflected at the interface and is split into its circularly polarized wave components. The transmitted ray (not shown) splits similar to the scheme shown in (a).

the two angles of refraction. The splitting needs to be large enough for it to be resolved on the detector. Fresnel showed that multiple refraction at nonparallel interfaces can be used to increase the net divergence [1,3]. Our experimental geometry, depicted in Fig. 2(a), makes use of this amplification scheme, and is similar to the one originally devised by Fresnel to image double refraction in optically active quartz crystals [1,3,8]. In Fig. 2(b) it is seen that the splitting of a 405 nm diode laser beam, traversing prismatic cuvettes filled with optically active solutions of limonene, increases with the number of interfaces and becomes clearly resolvable on a CCD camera. We verified that the two beams in Fig. 2(b) IV are indeed circularly polarized and that they are of opposite circularity. The refracted beams are of equal intensity, even though the path lengths of the two beams through the R and S liquids differ, as the differential absorption (circular dichroism) is negligible in limonene at 405 nm. Should the incident light be unpolarized, then the two circularly polarized refracted beams have no fixed phase relation [5]. If the incident light is plane polarized, then the two circularly polarized beams are coherent and could in principle be made to interfere by using suitable wave plates [5].

Multiple interfaces amplify the double-refraction effects, since the angular deviation increases with each interface, but they are not required in order to measure the chirality-induced splitting of a light beam, which may also be observed in reflection. In the case of reflection inside a liquid, as shown in Fig. 1(b), the angles can be obtained by considering the boundary conditions of the electromagnetic waves at the interface. The latter requires that the
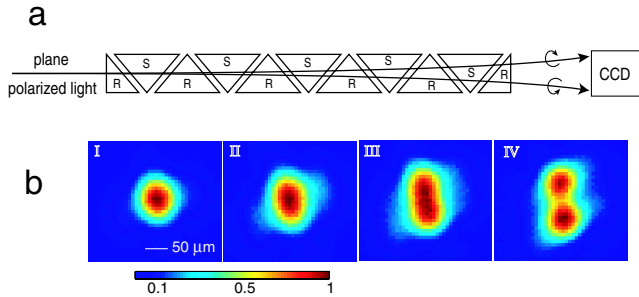

FIG. 2 (color online). (a) Schematic of the experimental geometry used to image double refraction. A plane polarized light ray is incident onto a stack of prismatic cuvettes, which are alternately filled with the R and S enantiomer of a chiral liquid. The angular divergence increases by $\sim 2\delta$ at each $R \setminus S$ or S/R interface, since both the order of the enantiomers and the orientation of the interface changes from one cuvette to the next. The beam would not split in an achiral liquid. (b) Intensity plots of a laser with Gaussian beam profile recorded on a CCD camera (4.6 μm pixel size). The images correspond to a passage through 8, 12, 16, and 20 interfaces, (labeled I–IV, respectively). Image IV clearly shows two well-separated Gaussian beam profiles that are right- (upper) and left- (lower) circularly polarized.
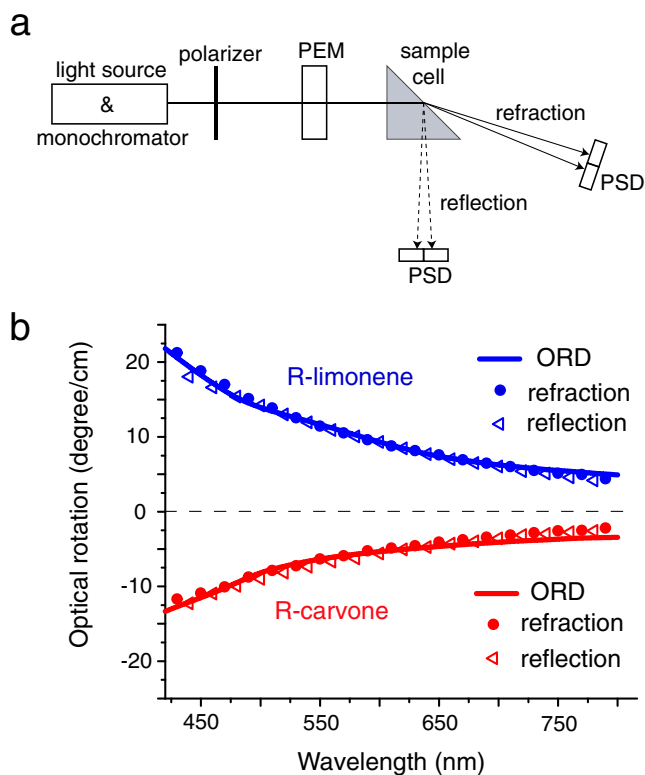
wave vectors of the incident $\vec{k}_i$ and the reflected beam $\vec{k}_r$ have the same tangential components along the interface, i.e., satisfy $k_i \sin\theta_i = k_r \sin\theta_r$, where the angle of reflection (measured from the interface normal) is θ_r, and where $k_r = 2\pi n_r/\lambda$ and n_r is the refractive index the reflected beam experiences. k_i is correspondingly defined for the incident beam. An ordinary achiral liquid is described by a single refractive index and it follows that the law of reflection ($\theta_r = \theta_i$) holds regardless of the polarization state of the light. Because a circularly polarized wave undergoes a (partial) polarization reversal upon reflection, the wave vectors for the incident and the reflected wave in a chiral liquid are associated with different refractive indices. Hence, in an optically active medium $\theta_r \neq \theta_i$, and there are two reflected waves with angles of reflection $\theta^{(-)}$ and $\theta^{(+)}$ [6,7,9]. Their angular divergence after reflection is given by

$$\delta' \approx \frac{\tan\theta_i}{n}(n^{(-)} - n^{(+)}). \qquad (3)$$

In general, the circular polarization components will not fully reverse their circularity upon reflection, but become elliptically polarized. The degree of circular polarization, and hence the fraction of the beam that doubly reflects, depends on the Fresnel reflection coefficients for a given interface, and needs to be accounted for in practice.

The divergence between the two circular components of a reflected or refracted beam can be directly compared with the optical rotation in radians developed by light at the wavelength λ traversing a distance d in a chiral liquid [2,10]:

$$\alpha = \frac{\pi d}{\lambda}(n^{(-)} - n^{(+)}), \qquad (4)$$

which is also a function of the circular birefringence $n^{(-)} - n^{(+)}$. It is thus expected that δ/λ and δ'/λ will exhibit the same dependence on wavelength as optical rotation does, provided the dispersion of the average refractive index of the chiral medium in Eqs. (2) and (3) has been accounted for.

To test this, we passed light from a Xe arc lamp through a monochromator and recorded δ and δ' as a function of wavelength. The setup is schematically depicted in Fig. 3(a). A photoelastic modulator is used to modulate the polarization of the light between left- and right-circularly polarized at ~ 50 kHz and the position of the light beam is synchronously recorded by a one-dimensional position sensitive detector (with spatial resolution of ~ 0.1 μm) and a lock-in amplifier. Figure 3(b) shows that the angular divergence measurements obtained in reflection as well as in refraction at a single interface between a chiral liquid and an achiral medium, are in complete agreement with the conventionally measured optical rotatory dispersion (ORD) spectrum. Our results show that reflection and refraction can be used in place of

FIG. 3 (color online). (a) Schematic of the experimental ge-
ometry used for the reflection and refraction measurements at a
single interface, a position sensitive diode (PSD) and a photo-
elastic modulator (PEM) are shown. In order to clearly separate
reflection and refraction phenomena, a 90° prismatic cuvette
holds the chiral liquid, so that the doubly reflected beam exits the
cuvette without doubly refracting. (b) Optical rotation and ORD
data obtained from the wavelength -dependence of the measured
angular divergence in both reflection (open triangles) and refrac-
tion (solid circles) at a single achiral-chiral interface for two
optically active liquids R-($-$)-carvone (symbols in red) and
R-($+$)-limonene (symbols in blue). The data are seen to be in
excellent agreement with conventional optical rotation measure-
ments obtained with a spectropolarimeter (corresponding solid
lines). The error bars of individual measurements are smaller
than the size of the symbols.

conventional optical rotation measurements, and their dis-
persion correspondingly in place of ORD for structural and
stereochemical studies. The reflection data confirm that the
"law of reflection" does not necessarily hold in the pres-
ence of chiral molecules. We have obtained similar results
with other optically active liquids, such as pinene and
aqueous glucose solutions.

  Away from the interface, the bulk of a liquid does not
affect reflection and refraction angles, and so it is interest-
ing to ask if it is indeed possible to miniaturize the sample
cell and hence the liquid volume without any loss of
sensitivity. In doing so an important aspect is the shape
of the liquid cell. The two circularly polarized (CP) com-
ponents will experience a small parallel displacement upon
traversing a thin slab geometry with parallel front and exit

windows, but will not experience any change in their
propagation directions. The parallel displacement scales
with the thickness of the fluid layer and this precludes
miniaturization. The reflection or refraction must therefore
take place in an asymmetric fashion, and in general, both
phenomena will contribute to the angular divergence be-
tween the CP beams. We have constructed a microcell
(inset of Fig. 4) where the liquid is confined asymmetri-
cally by a part of a cylindrical Fresnel lens. In Fig. 4 we
compare the results from double-refraction measurements
in the microcell where the average path length through the
chiral liquid is ~ 400 μm with results from a macroscopic
cuvette where the light propagates ~ 2 cm through an
optically active liquid. A polarimeter would record an
optical rotation in the microcell that is 50 times smaller
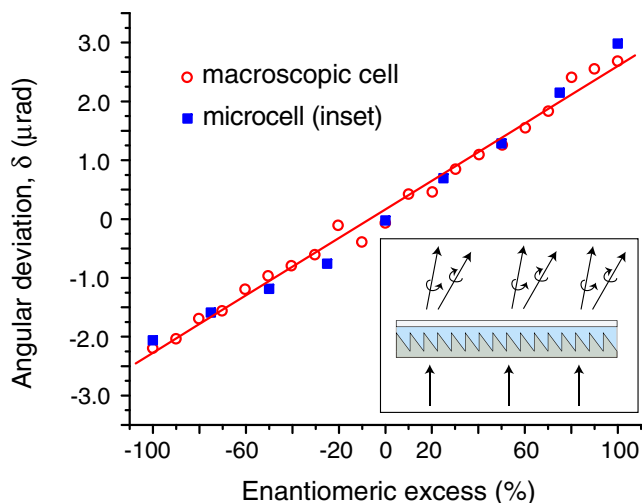than that of the macroscopic cell, yet in Fig. 4 it is clearly

FIG. 4 (color online). Angular divergence δ, measured in
refraction, as a function of the concentration difference between
the two enantiomers of limonene, denoted by R and S, respec-
tively. The enantiomeric excess is defined as the percent con-
centration difference between the enantiomers $\%[R] - \%[S]$.
The measurements are obtained at a single achiral-chiral inter-
face in two experimental geometries: a macroscopic cell (red
circles) and a microcell (blue squares), with average path lengths
of ~ 2 cm and ~ 400 μm, respectively. Each data point is
measured with a standard deviation of ~ 10 nrad and the straight
line is a guide to the eye. The experimental setup used in
conjunction with the microcell is shown in the inset: a thin
film of liquid passes through part of a commercial Fresnel lens
(height of 45° sawtooth-prisms ~ 700 μm), and a glass window
separated by a 40 μm spacer (not shown). The data sets have
been obtained with a 488 nm Ar$^+$ and a 405 nm diode laser and
have been normalized to 488 nm by scaling the measurements at
405 nm with the ratio of the respective circular birefringences.
The error bars of individual measurements are smaller than the
size of the symbols. However, the modulator itself gives rise to
an angular deviation ($\sim \mu$rad) that fluctuates on the time scale of
the measurement (~ 10 s) and causes the data points to deviate
from a straight line.

seen that the measurements of the microcell and the macroscopic cuvette give rise to the same angular divergences. Since the circular birefringence of the chiral medium is proportional to the concentration difference between the two enantiomers, it follows that the angular divergence must be of equal magnitude and of opposite sign as the solution changes its handedness, and must be zero for the racemic (50:50) mixture, as is observed for both cells.

An attractive feature of the interfacial refraction and reflection phenomena is that the sample volume can be reduced further. If the optical path length in the microcell is reduced to a few microns, then already a modest [11] angular resolution of 100 nrad (well within the current absolute accuracy of the setup used in Fig. 4) will make it possible to observe optical activities that are below the resolution limit of a standard laboratory polarimeter, i.e., $<0.001°$. Miniaturization of optical components to micrometer dimensions is expected to give rise to diffraction phenomena. This immediately raises the interesting question whether the circular differential reflection and refraction phenomena of this Letter can also be observed in diffraction. Under normal incidence, the angular position of the diffracted spot at order m for a diffraction grating with a groove spacing D is given by $D \sin\beta = (m\lambda)/n$, where n is the refractive index of the light in the medium where the diffraction grating is placed. Since the refractive indices of right and left circularly polarized light are different in an optically active medium ($n^{(\pm)}$), the angular positions of the diffracted spots are also expected to differ. We have made measurements with reflection gratings and found that a chiral diffraction effect exists, such that left- and right-circularly polarized components diffract with different angles of diffraction [12]:

$$D \sin\beta^{(\pm)} = (m\lambda)/n^{(\pm)}. \qquad (5)$$

We believe that these findings, together with our observation of double refraction and reflection in chiral liquids, will open new possibilities in the detection of optically active molecules in small sample geometries such as in thin films or microfluidic devices.

The unique optical properties of chiral media have also been considered as components in electromagnetic coatings and microwave devices [13], and more recently, in connection with negative index media [14,15]. Artificial structures such as chiral helices have been used to make optically active materials that give rise to relatively much larger optical rotations at microwave frequencies [16–18]. The double-refraction and reflection phenomena that we have observed in liquids are therefore expected to give rise

to correspondingly much larger angular divergences and splittings in chiral metamaterials.

Finally, it is interesting to note that a magnetic field renders any medium optically active, for a linearly polarized light wave propagating along the direction of the field will experience optical rotation. It thus follows that the Faraday effect can also be observed in reflection and refraction [12], similar to the chiral phenomena reported in this Letter.

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