Circular differential double diffraction in chiral media

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In an optically active liquid the diffraction angle depends on the circular polarization state of the incident light beam. We report the observation of circular differential diffraction in an isotropic chiral medium, and we demonstrate that double diffraction is an alternate means to determine the handedness (enantiomeric excess) of a solution. © 2007 Optical Society of America

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Fresnel showed that the difference in the refractive indices for left and right circularly polarized light underlies the optical rotation that is observed in optically active (chiral) liquids. Given that there are two refractive indices, Fresnel predicted that a light beam refracting into or out of a chiral liquid will not only change its direction of propagation, but should also separate into its two circularly polarized components [1,2]. It has come to our attention that Fleischl gave a description of an early experimental apparatus consisting of 22 prisms filled alternately with *leavorotatory* and *dextrorotatory* liquids (as first suggested by Fresnel [1]) that permitted him to see two images of a single pinhole when viewed with a magnifying objective [3]. The doubling of a laser beam traversing multiple chiral interfaces has recently been imaged on a CCD camera, and, moreover, it has been shown that the splitting of light in chiral media can also be observed in reflection and at a single interface [4]. Unlike optical rotation in transmission, reflection and refraction occurs within a few wavelengths at the interface. Observation of double refraction and reflection effects at a single interface, as opposed to optical rotation in transmission or imaging using multiple liquid cells, thus paves the way for miniaturization of optical activity measurements and makes their integration into microfluidic devices possible [4]. Miniaturization can lead to system dimensions that approach the wavelength of light, such that diffraction phenomena become important. This raises the question whether circular differential effects can be observed in diffraction. Diffraction in chiral media has been considered in a number of theoretical discussions (see, for instance, [5–8]). In addition, effects of chirality in the grating structures have been examined both analytically as well as experimentally [9–12]. Here we consider the optical response of an ordinary achiral grating that is placed in an optically active liquid. We show experimentally that in a chiral liquid the position of a diffraction order depends on the circular polarization state of the incident light. We also demonstrate that small differences in the diffraction angle can be resolved experimentally and that this is a measure of the solution's handedness.

Consider a plane reflection grating of groove spacing D immersed in a chiral liquid, as is schematically depicted in Fig. 1(a). Assuming that any circular polarization state reverses completely upon reflection, it follows that the incident and diffracted circular components are associated with different refractive indices. For example, if left circularly polarized light with corresponding refractive index $n^{(-)}$ is incident onto the grating with angle of incidence α, it diffracts at order m with angle $\beta_m^{(+)}$ and is characterized by the refractive index $n^{(+)}$. The diffraction equation in an isotropic chiral medium is given by

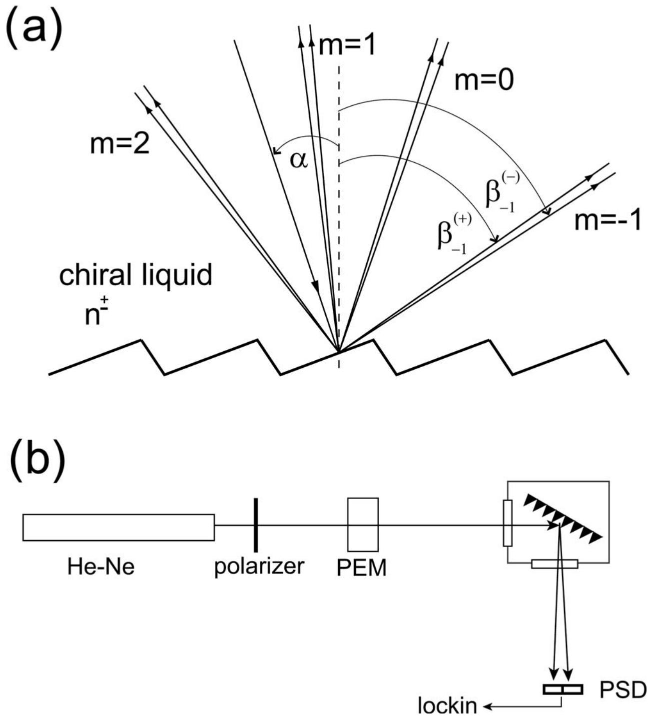

Fig. 1. Diffraction at a reflection grating immersed in a chiral liquid. (a) Linear or unpolarized incident beam is shown to split into its two circular polarization components at each diffraction order. The splitting is of opposite sign for the mirror-image liquid (enantiomer) and vanishes in an achiral system. (b) Experimental arrangement used for the diffraction measurements. A rectangular liquid cuvette holds a reflection grating.

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$$n^{(\mp)}\sin(\alpha)-n^{(\pm)}\sin(\beta_m^{(\pm)})=\frac{m\lambda}{D}. \tag{1}$$

Experimentally, we will measure the difference in the angles of diffraction for the two circular polarization states, $\delta_m=\beta_m^{(+)}-\beta_m^{(-)}$. If we define β_m as the mean of the two diffraction angles $\beta^{(+)}$ and $\beta^{(-)}$, with $\beta_m=\sin^{-1}[m\lambda/(nD)-\sin\alpha]$, then for small δ_m

$$\sin(\beta_m\pm\delta_m/2)\approx\sin\beta_m\pm\frac{\delta_m}{2}\cos\beta_m, \tag{2}$$

and given that in all optically active liquids the circular birefringence $n^{(-)}-n^{(+)}$ is much smaller than the average refractive index $n=(n^{(-)}+n^{(+)})/2$, the difference in the diffraction angles may finally be written as

$$\delta_m=\frac{n^{(-)}-n^{(+)}}{n}\left(\frac{\sin\alpha}{\cos\beta_m}+\tan\beta_m\right). \tag{3}$$

The experimental geometry is shown in Fig. 1(b) and is devised such that the incident and diffracted beams are, respectively, normal to the entrance and exit windows of the liquid cuvette. This eliminates potential artifacts due to double refraction. The reflection grating is suspended in the liquid and mounted on a rotation stage so that different diffraction orders can be selected by rotating the grating, while keeping $\alpha+\beta_m=\pi/2$ for all values of m. For the particular experimental geometry described here, Eq. (3) can therefore be simplified to

$$\delta_m\simeq\frac{n^{(-)}-n^{(+)}}{n}\left(1+\tan\beta_m\right). \tag{4}$$

The polarization of the incident light at 633 nm (He–Ne laser) is modulated between right and left circularly polarized at ~47 kHz with a photoelastic modulator (PEM), and the position of the diffracted beam is synchronously recorded by a 1-D position-sensitive diode (PSD) and a lock-in amplifier. The fixed distance from the grating to the detector (~0.8 m) is used to convert the lock-in signal to the angular divergence δ_m. The experiments are conducted with a blazed reflection grating (Edmund Optics, $D=600$ lines per millimeter, blaze angle 28°41′) and a symmetric grating (1200 lines per millimeter, results not shown). The relative percentage of the left- and the right-handed forms of a liquid, such as limonene, carvone, or pinene, are then changed, while the difference in diffraction angles $\beta_m^{(+)}-\beta_m^{(-)}$ is recorded. The results are shown in Fig. 2 and are in good agreement with the simple theory presented in Eq. (4). It is seen that the angular divergence varies linearly with the enantiomeric excess (percent concentration difference between the two mirror-image forms of the liquid). Further, the ratio of the angular divergence in limonene to carvone is approximately equal to the ratio of their specific optical rotations (including sign reversal). Double diffraction is thus an alternate means to determine a chiral liquid's circular birefringence $n^{(-)}-n^{(+)}$, which is of opposite sign for the two handed forms of a chiral molecule. For any particular diffraction order, we find that the measurements make it possible to resolve small changes in enantiomeric excess (optical purity) of less than 1%.

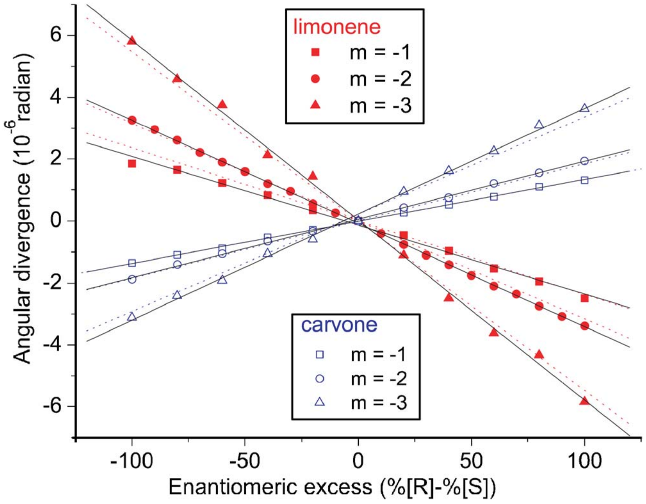

Fig. 2. (Color online) Difference in the diffraction angles for left- and right-circularly polarized light. The angular deviation is recorded for each diffraction order in carvone and limonene as a function of the liquid's enantiomeric excess, which is defined as the percent concentration difference between the two mirror-image forms of the liquid, denoted as R and S, respectively. The straight lines are from a fit to the experimental data, and the dotted lines are from theory.

In deriving Eq. (4), we have assumed that the circular-polarized-light states reverse perfectly upon diffraction. However, in practice, it is found that the diffracted beams are elliptically polarized. For the two gratings used in the course of our experiments, we found that the circular beams were between 24% and 92% linearly polarized upon diffraction. It is therefore surprising that the experimental data agree so well with the simple theory presented in Eq. (4). To explain the relative insensitivity to the depolarization of the circular components may thus require a more sophisticated theoretical model, presumably one that calculates angles of diffraction with consideration of the Fresnel reflection coefficients [13] for the particular grating surface.

In summary, we present experimental results on diffraction of light in a chiral liquid. We show that the left and right circularly polarized light components have different angles of diffraction. The angular divergence between the two circular components is a direct measure of the enantiomeric excess (optical purity) of the medium and could prove useful in detecting chiral molecules in small liquid volumes.

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