Ring-resonator-based frequency-domain optical activity measurements of a chiral liquid

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Chiral liquids rotate the plane of polarization of linearly polarized light and are therefore optically active. Here we show that optical rotation can be observed in the frequency domain. A chiral liquid introduced in a fiber-loop ring resonator that supports left and right circularly polarized modes gives rise to relative frequency shifts that are a direct measure of the liquid's circular birefringence and hence of its optical activity. The effect is in principle not diminished if the circumference of the ring is reduced. The technique is similarly applicable to refractive index and linear birefringence measurements. © 2006 Optical Society of America

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Natural optical activity arises because a medium has different refractive indices for left (−) and right (+) circularly polarized light. The optical rotation, in radians, developed over a path length l is a function of the wavelength λ and is given by

$$\theta = \frac{\pi l}{\lambda}[n^{(-)} - n^{(+)}]. \tag{1}$$

The circular birefringence, $n^{(-)} - n^{(+)}$, is, however, even in a pure chiral liquid small and at most a few parts in 10^6. It is thus desirable to increase the effective path length through the optically active medium without the need for large sample volumes. This can be achieved in an optical cavity as long as one ensures that the optical rotation does not cancel on the round trip, which in practice one can accomplish by placing quarter-wave plates in the cavity.[1] Significant enhancements in sensitivity compared with single-pass instruments have been reported for measurements that make use of Fabry–Perot resonators,[1–3] including polarization-sensitive implementations of cavity-ringdown spectroscopy,[4,5] as well as laser cavities.[6,7] Both single-pass and multipass techniques typically determine the rotation in Eq. (1) via intensity measurements that either require rotating polarization optics or separate the orthogonally polarized components of the light and therefore require a balanced detection scheme.

In this Letter we show that circular birefringence (optical rotation) can also be determined by frequency measurements. Left and right circularly polarized modes acquire unequal phases when a chiral liquid is introduced into a resonator such that their resonance frequencies shift relative to each other. We demonstrate the method, using a fiber optic ring resonator in combination with a narrow-linewidth cw laser.

A fiber-loop resonator[8,9] may be considered to be a fiber- or waveguide-based Fabry–Perot resonator that consists of a closed fiber loop in contact with a linear waveguide via a variable (directional) coupler. A resonance in the ring requires that the optical path length be a multiple of the wavelength of the light. Resonances are observed as minima in a transmission spectrum whenever an integral multiple of the wavelength in the ring equals the circumference of the fiber loop. A shift in the resonance wavelength occurs if either the path length or the refractive index changes. Refractive indices may be measured by tuning the frequency of a laser with a sufficiently narrow linewidth.

Introduction of a sample with refractive index n_s into the ring resonator will cause a wavelength shift of the resonances relative to the reference medium with refractive index n_0, which may, for instance, be air:

$$\frac{\Delta\lambda}{\lambda} = \frac{n_s - n_0}{n_{\text{eff}}} f, \tag{2}$$

where f is the fraction of the total ring circumference that contains the optically active sample. n_{eff} is an effective refractive index used to describe the entire fiber-loop resonator in the presence of the reference medium and corresponds to the round-trip phase $2\pi n_{\text{eff}} L/\lambda$ acquired by a resonant mode at wavelength λ, where the circumference (fiber and free-space part) is L.

The inherent birefringence of a bent optical fiber will in general give rise to resonant modes with different polarization states.[10] These modes may be used to generate circularly polarized modes that are sensitive to chirality. A wavelength shift that is equal in magnitude and opposite in sign for the two circularly polarized modes is a direct function of the liquid's circular birefringence and hence of its optical activity. Thus, particular interest are relative changes in the resonance wavelengths of a pair of left and right circularly polarized modes centered at λ:

$$\left|\frac{\Delta\lambda^{(-)} - \Delta\lambda^{(+)}}{\lambda}\right| = \frac{n^{(-)} - n^{(+)}}{n_{\text{eff}}} f, \tag{3}$$

where any common mode noise is automatically eliminated. It can also be seen that the equation describing optical activity in a ring resonator is independent of the actual dimension of the ring. For a given finesse and a given fraction f, a reduction in the size of the ring does not lead to a loss of sensitivity.

This is in contrast to all conventional polarimetric techniques that are based on Eq. (1). The favorable scaling of a ring resonator could be promising for measurements of enantiomeric (mirror image) excess that require small sample volumes.

The absolute sign of the shift in Eq. (3) depends on the ordering of the circularly polarized modes; e.g., for a positive birefringence the spacing between two modes increases if $\lambda^{(-)} > \lambda^{(+)}$.

The experimental setup is schematically depicted in Fig. 1. The ring resonator is formed by a loop of single-mode optical fiber that is evanescently coupled to a bus waveguide by means of a variable coupler.[8] An ~20 cm section of the fiber loop has been replaced with a U bench that contains collimators and a provision for holding a 10 cm liquid cuvette. The collimated beam size is ~2 mm. A 40 mW tunable distributed-feedback laser operating at ~763 nm is directly coupled to the linear waveguide. We tune the laser by ramping the diode current with a sawtooth-shaped function and typically scan the wavelength by 5 to 6 pm while acquiring 1000 points with a computer. The laser diode tuning coefficient is 0.0019 nm/mA and has been determined with a wavelength meter. Resonances appear as Lorentzian-shaped dips[9] in the transmission spectrum recorded by an InGaAs photodetector (D1 in Fig. 1). The intensity extinction and the widths of the resonances depend, among other factors, on the coupling ratio.[9,11] Figure 2 shows transmission spectra for an open fiber-loop ring resonator with an ~50 cm circumference. The half-wave plate before the coupler is used to excite one or both eigenpolarizations of the fiber-loop resonator.[12] Our measurements make use of both eigenpolarizations. A quarter-wave plate, which is placed before the liquid cell, transforms the quasi-linear modes into left-circularly polarized and right circularly polarized modes for the passage through the liquid. A second quarter-wave plate, which has its fast axis parallel to the first one, is placed after the liquid and restores the linear polarization of the modes. Insertion of a beam splitter allows some of the light to be projected onto photodetector D2 via a polarization analyzer arrangement (Fig. 1).

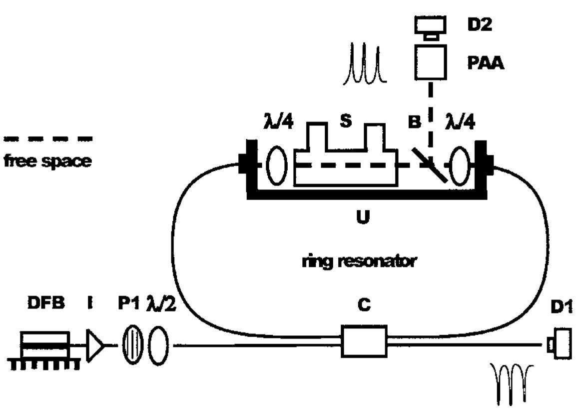

Fig. 1. A tunable ~763 nm distributed-feedback (DFB) laser is coupled to a bus waveguide via an optical isolator (I). The ring resonator has a circumference of ~50 cm. A polarizer (P1) and a half-wave plate (λ/2) control the polarization of the light before the variable-ratio coupler (C). The U bench (U) connected via fiber ports holds two quarter-wave plates (λ/4's) and a 10 cm sample cell (S). Resonances are observed as either dips in the transmission spectrum with photodetector D1 or as peaks with photodetector D2. The polarization states of the modes in the ring can be analyzed after beam splitter (B) with polarization analyzer arrangement (PAA), which consists of a suitable combination of wave plates and polarizers.

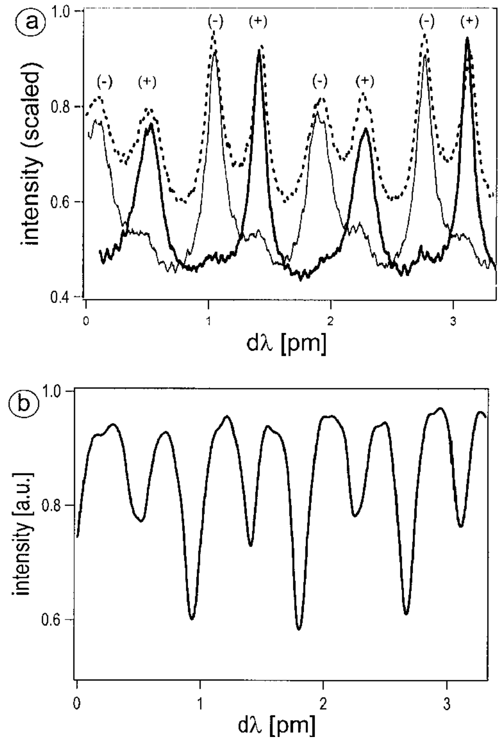

Fig. 2. (a) Transmission spectra (raw data) of limonone and a wavelength scan of ~763 nm+dλ recorded by photodetector D2 (see Fig. 1). Spectra are shown after polarization analysis for either left (−) or right (+) circularly polarized modes (respectively, thin and thick solid curves) or for a scan without polarization analysis (dotted curve). For details see text. (b) Corresponding transmission spectrum (raw data) recorded with photodetector D1 (Fig. 1).

We note that a ring resonator can thus also function as a high-frequency source of polarization-modulated light at D2, as the laser diode can be tuned between two or more resonant wavelengths of orthogonally polarized eigenmodes at megahertz to possibly gigahertz frequencies.

Figure 2(a) confirms that the modes traversing the cuvette are indeed circularly polarized and spectrally separated. Modes of opposite circularity acquire different phases, and hence their resonance wavelengths shift relative to each other.

To be able to demonstrate the method of frequency-domain optical rotation measurements by use of the fiber-loop resonator depicted in Fig. 1, wavelength shifts that correspond to birefringences of $\sim 10^{-6}$ need to be resolvable. From Fig. 2 it can be seen that each set of orthogonally polarized modes shows resonances separated by a free spectral range of ~0.85 pm and with a linewidth of ~0.25 pm (Fig. 2). The optical losses in the open fiber-loop resonator containing a sample cell are significant. Nevertheless, the recorded finesse of ~3.4 already permits the

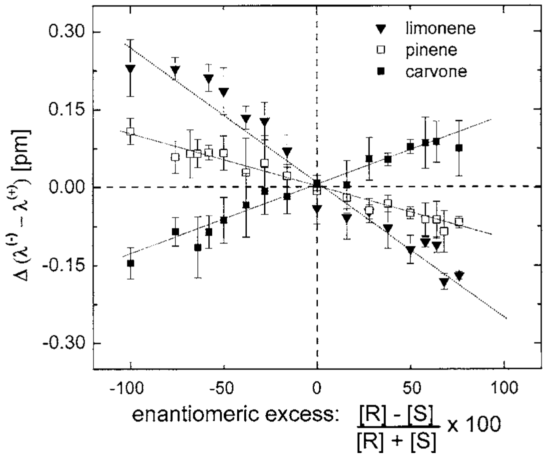

Fig. 3. Change in the spacing of left (−) and right (+) circularly polarized resonant modes as a function of the enantiomeric excess. [R] and [S], respectively, denote the concentrations of the liquids' R and S enantiomers. The lines are linear fits to the data.

detection of relative wavelength shifts of ~0.02 pm (1/10 of the linewidth), and from Eq. (2) it follows that this corresponds to refractive-index changes (data not shown) and birefringences of $\sim 2\times 10^{-7}$, i.e., rotations of ~4° in a 10 cm cuvette. The setup does not yet include the active tracking of resonances under feedback, or modulation techniques, which would immediately enhance the sensitivity. A significant further increase in finesse and therefore in sensitivity can be expected if the optical losses are compensated for, e.g., by optical amplification. This was demonstrated by Okamura and Iwatsuki, who report a finesse of >500 for a fiber-loop resonator that contained a section of pumped erbium-doped fiber.[13]

We have observed the wavelength shifts of resonances that are due to optical activity for three chiral liquids: limonene, pinene, and carvone (Sigma-Aldrich). The birefringence (optical rotation) of an optically active liquid and its enantiomer are equal in magnitude and opposite in sign. For a 50:50 (racemic) mixture the solution is no longer optically active and the birefringence is accordingly zero. We vary the enantiomeric excess (percent optical activity) of the liquids by titrating the appropriate amounts of the two enantiomers, denoted R and S. The observed relative wavelength shifts are shown in Fig. 3, where the difference in resonance wavelengths of two adjacent left and right circularly polarized modes is recorded as a function of the enantiomeric excess. The relative wavelength shift of the resonances varies linearly with enantiomeric excess and is zero for the racemic mixture. In accordance with optical rotation data, the circular birefringence of carvone is of opposite sign to that of limonene and pinene.

In summary, we have shown that optical rotation of a chiral liquid can be observed from the relative shifts of resonance frequencies associated with circularly polarized modes in a resonator. The scheme is demonstrated by insertion of a liquid cell directly into a fiber-loop ring resonator. The relative wavelength shifts of the left and right circularly polarized light modes are independent of the actual dimension of the ring, which is promising for device miniaturization and the analysis of small sample volumes. The frequency-domain optical rotation measurements presented in this Letter could be implemented in other resonators (cavities) and could also be used to determine magneto-optical rotations and linear birefringences, as well as refractive indices.

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