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Optics Communications 218 (2003) 317–323
OPTICS COMMUNICATIONS
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A new method for measuring the chiral parameter and the average refractive index of a chiral liquid

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Received 10 July 2002; received in revised form 15 January 2003; accepted 23 January 2003

Abstract

We designed a method for measuring chiral parameter and average refractive index of an isotropic chiral medium using critical angle phenomena. Linearly polarized light is guided to project onto the interface of a semi-spherical glass and a chiral liquid. The reflected light passes through an analyzer to extract the interference signal of s- and p-polarization lights. Their phase difference is first optimized by a suitable optical arrangement and subsequently measured by a heterodyne interferometer. The result, then, is fed into equations to estimate the chiral parameter. We determine the average index of refraction from the critical angle occurred at the discontinuity of the phase difference of two polarized lights. Our method of measurement has the implicational merits of both common-path interferometry and heterodyne interferometry.

1. Introduction

Optical activity (gyrotropy) is a property of the non-centrosymmetric media of chiral structural elements. An isotropic chiral liquid is described by Drude–Born–Fedorov constitutive relations [1–4] (in Gaussian units)

$$\vec{D} = \varepsilon[\vec{E} + \beta\nabla \times \vec{E}], \tag{1a}$$

$$\vec{B} = \mu[\vec{H} + \beta\nabla \times \vec{H}], \tag{1b}$$

where β is the gyrotropy, ε the average dielectric constant and μ the permeability. Through use of Maxwell's equations, and assumption of plane-wave solutions of frequency ω_0 and wave vector $\vec{k} = k\hat{k}$, Eqs. (1a) and (1b) can be expressed as follows:

$$\vec{D} = \varepsilon\left[\vec{E} + \mathrm{i}f(\vec{k} \times \vec{E})/nk_0\right], \tag{2a}$$

$$\vec{B} = \mu\left[\vec{H} + \mathrm{i}f\left(\vec{k} \times \vec{H}\right)/nk_0\right], \tag{2b}$$

where $k_0 = \omega_0/c$, $n = \sqrt{\varepsilon\mu}$ is the average refractive index and $f = (\varepsilon\mu)^{-1/2}k_0\beta$ provides a convenient measure of the gyrotropy of the medium.

If n_+ and n_- are the refractive indices of the left- and the right-circularly polarized lights in the chiral liquid, then we have $n_\pm = n \pm g$. Here, g is the chiral parameter. In addition, g can be expressed as $g = nf$. The chiral parameter is ordinarily very much less than unity ($g \approx 10^{-4} \sim 10^{-7}$) for many organic and inorganic materials.

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0030-4018/03/$ - see front matter
doi:10.1016/S0030-4018(03)01183-0

A chiral parameter and an average refractive index are important characteristic constants of a chiral liquid [5]. The chiral parameter is so smaller ($\ll 1$) that its effect on the amplitude and the phase of the light reflected from the chiral liquid are nearly unnoticeable. Therefore, almost all of the previous methods measured the light transmitted through a chiral liquid to estimate its chiral parameter [6–9]. These transmission methods required relative larger amount of liquid to make the chiral parameter measurable. Although many methods were proposed for measuring the average refractive index, to the best of our knowledge, there is no single optical setup that can measure the chiral parameter and the average refractive index simultaneously. To get around of this point we present, an alternative method for measuring the chiral parameter and the average refractive index of a chiral liquid in one single optical configuration. Linearly polarized light is incident on the interface between a glass semi-sphere and a chiral liquid. The reflected light passes through an analyzer and the desired polarizing components are extracted to interfere. If the incident angle is slightly smaller than the critical angle and the polarization plane of the incident light is nearly orthogonal to the transmission axis of the analyzer, then the phase difference between s- and p-polarizations of the reflected light will be enhanced from 2 to 4 orders of magnitude, and thus becomes measurable by a heterodyne interferometry [10,11]. Substituting the measured result into specially derived equation Eq. (15) (infra vide), the chiral parameter can be estimated. In addition, this phase difference changes abruptly as the incident angle is approaching the critical angle. This limiting angle then is taken to be the critical angle. Consequently, the average refractive index can be calculated. In addition, our method is benefited from the advantages of the common-path interferometry and the heterodyne interferometry.

2. Principle

The schematic diagram of this method is shown in Fig. 1(a). For convenience, the $+z$-axis is chosen to be along the direction of light propagation and the x-axis goes into the paper plane perpendicularly. A beam of linearly polarized laser light passes through a half-wave plate H, whose polarization plane is θ_p to the x-axis. Its Jones vector can be written as

$$E_i = \begin{pmatrix} \cos\theta_p \\ \sin\theta_p \end{pmatrix}. \quad (3)$$

This linearly polarized light passes through an electro-optic modulator (EO) with the fast axis lying along the x-axis. An external sawtooth voltage signal from a driver consisting of a linear

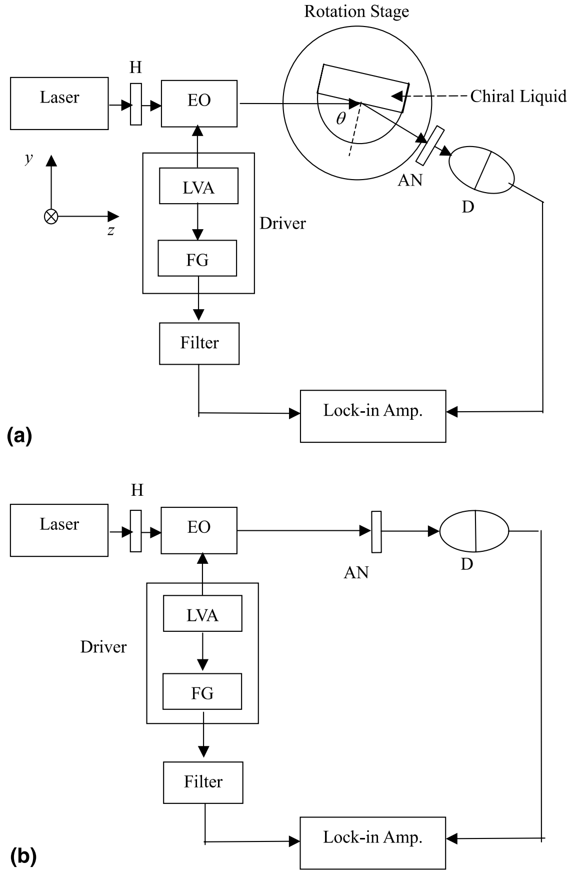


Fig. 1. Schematic diagrams for measuring (a) the phase difference owing to reflection at the interface between a glass hemisphere and a chiral liquid and (b) the initial phase difference of the reference signal. H, half-wave plate; EO, electro-optic modulator; LVA, linear voltage amplifier; FG, function generator; AN, analyzer; D, detector.

voltage amplifier (LVA) and a function generator (FG) is applied to the EO. Its angular frequency and amplitude are ω and $V_{\lambda/2}$ (half-voltage of EO), respectively. The phase retardation produced by the EO can be expressed as ωt, and the Jones vector of the light becomes

$$E_{\mathrm{i}}' = EO(\omega t)\cdot E_{\mathrm{i}} = \begin{pmatrix} \mathrm{e}^{\mathrm{i}\omega t/2} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}\omega t/2} \end{pmatrix}\begin{pmatrix} \cos\theta_{\mathrm{p}} \\ \sin\theta_{\mathrm{p}} \end{pmatrix} = \begin{pmatrix} \cos\theta_{\mathrm{p}}\cdot \mathrm{e}^{\mathrm{i}\omega t/2} \\ \sin\theta_{\mathrm{p}}\cdot \mathrm{e}^{-\mathrm{i}\omega t/2} \end{pmatrix}. \tag{4}$$

The light penetrates into a glass semi-sphere of refractive index n_0 with incident angle θ onto the interface between the semi-sphere and the chiral liquid. The light reflected from this interface passes through an analyzer AN with the transmission axis being at α with respect to the x-axis, and enters a photodetector D. Consequently, the Jones vector of the light becomes

$$\begin{aligned} E_{\mathrm{t}} &= \mathrm{AN}(\alpha)T_{\mathrm{ag}}(0^\circ)\cdot S(R)\cdot T_{\mathrm{ga}}(0^\circ)\cdot E_{\mathrm{i}}' \\ &= \begin{pmatrix} \cos^2\alpha & \sin\alpha\cos\alpha \\ \sin\alpha\cos\alpha & \sin^2\alpha \end{pmatrix}\begin{pmatrix} t_0' & 0 \\ 0 & t_0' \end{pmatrix} \cdot \begin{pmatrix} r_{11} & r_{12} \\ r_{21} & r_{22} \end{pmatrix}\cdot\begin{pmatrix} t_0 & 0 \\ 0 & t_0 \end{pmatrix} \cdot \begin{pmatrix} \cos\theta_{\mathrm{p}}\cdot \mathrm{e}^{\mathrm{i}\omega t/2} \\ \sin\theta_{\mathrm{p}}\cdot \mathrm{e}^{-\mathrm{i}\omega t/2} \end{pmatrix} \\ &= \left[A\mathrm{e}^{\mathrm{i}((\omega t/2)+\delta_1)} + B\mathrm{e}^{-\mathrm{i}((\omega t/2)-\delta_2)}\right]\cdot\begin{pmatrix} \cos\alpha \\ \sin\alpha \end{pmatrix}, \end{aligned} \tag{5}$$

where $S(R)$ is the Jones matrix of the chiral liquid as the light is reflected from it, and $T_{\mathrm{ga}}(0^\circ)$ and $T_{\mathrm{ag}}(0^\circ)$ are Jones matrices, t_0 and t_0' are transmission coefficients, as the light propagates from the air to the glass semi-sphere and vice versa, respectively. Although the chiral liquid has a weak light-induced effect of magnetization, it may be treated as an intrinsically non-magnetic material. Hence its permeability is nearly equivalent to unity. Based on Drude–Born–Fedorov constitutive relations, Maxwell's equations and electrodynamic boundary conditions, the chiral reflection coefficients r_{11}, r_{12}, r_{21} and r_{22} can be expressed as [12,13]

$$r_{11} \cong \left[(n/n_0)^2\cos\theta - q_1\right]/\left[(n/n_0)^2\cos\theta + q_1\right], \tag{6a}$$

$$r_{22} \cong (\cos\theta - q_1)/(\cos\theta + q_1), \tag{6b}$$

$$r_{12} = -r_{21} = \frac{\mathrm{i}\left[(n/n_0)^2(z_+ - z_-)\cos\theta\right]}{\left[(\cos\theta + q_1)\left\{(n/n_0)^2\cos\theta + q_1\right\}\right]}, \tag{6c}$$

respectively; and

$$q_1 = \left[(n/n_0)^2 - \sin^2\theta\right]^{1/2}, \tag{6d}$$

$$z_\pm = \cos\theta_\pm, \tag{6e}$$

$$z_+ - z_- \cong 2n_0 g\sin^2\theta/n^2 q_1, \tag{6f}$$

$$A = t_0' t_0\cos\theta_{\mathrm{p}}\cdot\sqrt{(r_{11}\cos\alpha)^2 - (r_{21}\sin\alpha)^2}, \tag{7a}$$

$$B = t_0' t_0\sin\theta_{\mathrm{p}}\cdot\sqrt{-(r_{12}\cos\alpha)^2 + (r_{22}\sin\alpha)^2}, \tag{7b}$$

$$\delta_1 = \mathrm{Arg}(r_{11} + r_{21}\cdot\tan\alpha), \tag{7c}$$

$$\delta_2 = \mathrm{Arg}(r_{22} + r_{12}\cdot\cot\alpha), \tag{7d}$$

where $\theta_\pm$ represent the refractive angles of the left- and the right-circularly lights in the chiral liquid [9] as shown in Fig. 2. Hence, the intensity measured by D is

$$I_{\mathrm{t}} = |E_{\mathrm{t}}|^2 = A^2 + B^2 + 2AB\cos(\omega t + \phi), \tag{8}$$

where ϕ is given as

$$\phi = \delta_1 - \delta_2 = \mathrm{Arg}(r_{11} + r_{21}\cdot\tan\alpha) - \mathrm{Arg}(r_{22} + r_{12}\cdot\cot\alpha). \tag{9}$$

Here, I_{t} is the test signal. On the other hand, the electrical signal generated by the function generator FG is filtered and becomes the reference signal. So, the reference signal has the form of

$$I_{\mathrm{r}} = I[1 + \cos(\omega t + \phi_{\mathrm{r}})], \tag{10}$$

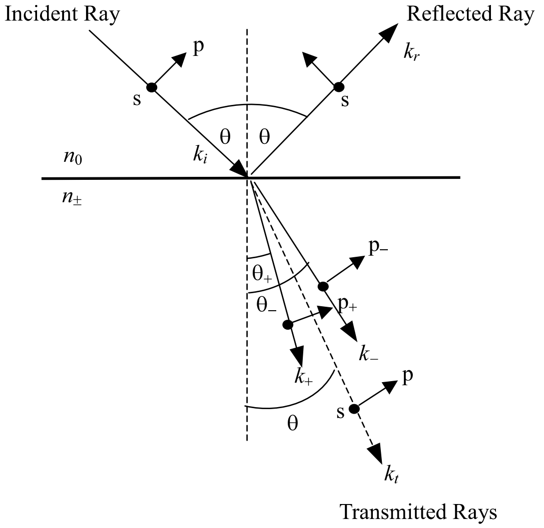


Fig. 2. Geometry of chiral reflection. k_t: wave vector of predicted transmitted ray in the absence of chirality.

where ϕ_r is the initial phase. These two sinusoidal signals are sent to a lock-in amplifier, as shown in Fig. 1(a). The phase difference between the reference signal and test signal,

$$\phi' = \phi - \phi_r \tag{11}$$

can be obtained. In the second measurement, the test beam is allowed to enter the photodetector D directly without the reflection at the interface between the glass semi-sphere and the chiral liquid, as shown in Fig. 1(b). The test signal still has the form of Eq. (8), but in this time with $\phi = 0$. Therefore the lock-in amplifier in Fig. 1(b) represents $-\phi_r$. Substituting $-\phi_r$ into Eq. (11), we can obtain the phase difference ϕ. Then, substituting Eqs. (6a)–(6f) into Eq. (9), we have

$$\begin{aligned}\phi &\cong -\tan^{-1}(M_1 g \tan\alpha) - \tan^{-1}(M_2 g \cot\alpha)\\ &= \tan^{-1}\left(\frac{-(M_1\tan\alpha + M_2\cot\alpha)g}{1 - M_1 M_2 g^2}\right),\end{aligned} \tag{12}$$

where

$$M_1 = \frac{\sin 2\theta \cdot \sin\theta}{n_0 q_1\Big((\cos\theta + q_1)\big[(n/n_0)^2\cos\theta - q_1\big]\Big)}, \tag{13a}$$

and

$$M_2 = \frac{\sin 2\theta \cdot \sin\theta}{n_0 q_1\Big((\cos\theta - q_1)\big[(n/n_0)^2\cos\theta - q_1\big]\Big)}. \tag{13b}$$

As θ is slightly smaller than the critical angle θ_c, we obtain $M_1 \cong M_2$. In general, the parameter g of a chiral liquid is smaller than 10^{-4}, and the values M_1 and M_2 are in the range of 10–10^3. So we have the condition $M_1 M_2 \cdot g^2 \ll 1$. Hence Eq. (12) can be written as

$$\begin{aligned}\phi &\cong \tan^{-1}[-(M_1\tan\alpha + M_2\cot\alpha)g]\\ &= \tan^{-1}\left\{-\frac{\sin 2\theta\sin\theta\cdot g}{n_0 q_1}\right.\\ &\quad\times\left[\frac{\tan\alpha}{(\cos\theta + q_1)\Big((n/n_0)^2\cos\theta - q_1\Big)}\right.\\ &\quad\left.\left.+\frac{\cot\alpha}{(\cos\theta - q_1)\Big((n/n_0)^2\cos\theta + q_1\Big)}\right]\right\}.\end{aligned} \tag{14}$$

Under this condition, if α is so chosen near 0 or 90°, then $|\phi|$ has an extreme value. Although ϕ is independent of ϕ_p, it is obvious from Eqs. (7a) and (7b) that the contrast of the test signal depends on ϕ_p. To enhance the contrast of the test signal, either the following two conditions should be chosen: (i) α is near 0° and θ_p is near 90°; (ii) α is near 90° and ϕ_p is near 0°. Consequently, Eq. (14) can be rewritten as

$$\begin{aligned}g \cong -\frac{n_0 q_1\tan\phi}{\sin 2\theta\sin\theta}&\left[\frac{\tan\alpha}{(\cos\theta + q_1)\Big((n/n_0)^2\cos\theta - q_1\Big)}\right.\\ &\left.+\frac{\cot\alpha}{(\cos\theta - q_1)\Big((n/n_0)^2\cos\theta + q_1\Big)}\right]^{-1}.\end{aligned} \tag{15}$$

It is seen from Eq. (15) that if n and ϕ are specified, then g can be calculated with the measurement of ϕ.

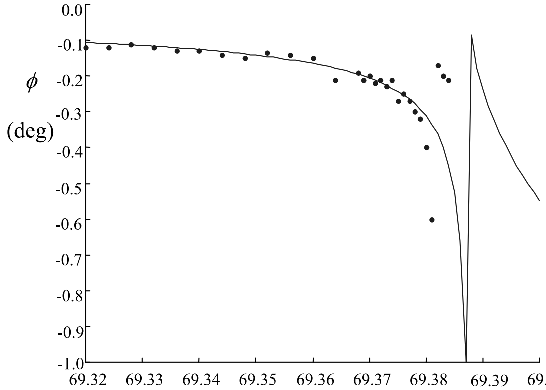
According to Snell's law, we obtain $n_+ = n_0\sin\theta_{c+}$, and $n_- = n_0\sin\theta_{c-}$, where θ_{c+} and θ_{c-} represent the critical angles of left- and right-circularly polarized lights. Since the difference $(n_+ - n_-)$ is extremely small, we have the condition $\theta_{c+} \cong \theta_{c-} \cong \theta_c$, where θ_c is the critical angle associated to the average refractive index. According to Eq. (14), we can see that ϕ will be changed abruptly as $\theta \cong \theta_c$. Based on this fact, θ_c can be measured accurately. Substituting this data into the following equation:

$$n = n_0 \sin\theta_c, \tag{16}$$

n can be obtained.

3. Experiments and results

In order to show the validity of this method, a He–Ne laser with 632.8 nm wavelength and an EO (Model 4002 Broadband, Newfocus) with a half-wave voltage 156 V were used to measure a 50% (wt%) glucose solution and a 50% (wt%) saccharose solution. The frequency of the sawtooth signal applied to the EO was 1 kHz. A BK7 glass semi-sphere with 1.51509 refractive index and the tested chiral liquid were mounted together on a high-precision rotation stage (Model M-URM100PP, Newfocus) with an angular resolution 0.001°. A locked-in amplifier (Model SR850, Stanford) with an angular resolution 0.001° was used to measure the phase difference. The experiments were operated at $\theta_p = 4°$, $\alpha = 88°$ and with at room temperature 21 °C. First, the tested chiral liquid was rotated slowly to identify the critical angle θ_c. Next, ϕ was measured with a 0.001° angular step from the incident angle θ, which is slightly small than the critical angle θ_c. Their measurement results and theoretical results shown in Figs. 3(a) and (b), respectively; where · denotes the measured data, and the solid lines are depicted by substituting the reference values n_{ref} and g_{ref} into Eq. (14). The reference values n_{ref} are obtained from [14], and g_{ref} can also be calculated with the following equation [15]:



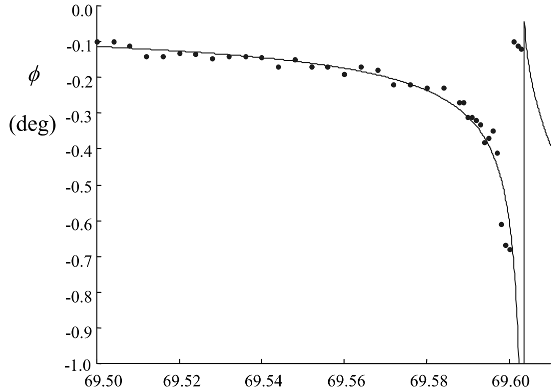


Fig. 3. Measurement results and theoretical curves of ϕ versus θ of (a) a 50% glucose solution and (b) a 50% saccharose solution, respectively.

$$[\alpha_s] = \frac{\theta\ (\text{deg})}{C_v \cdot L\ (\text{dm})} = \frac{(2\pi/\lambda)\cdot g_{ref}\cdot L\ (\text{m})\cdot(180/\pi)}{C_v \cdot L\ (\text{dm})} = \frac{(36/\lambda) g_{ref}}{C_v}, \tag{17}$$

where C_v (g/cm^3) is the volume concentration, $[\alpha_s]$ (deg/(dm g/cm^3)) the specific rotation (taken

Table 1
Experimental results and the corresponding reference data

Solution	θ	ϕ	$g(\times 10^7)$	$g_{ref}(\times 10^7)$	θ_c	n	n_{ref}
Saccharose ($C_w = 50\%$)	69.548°	−0.160°	6.4	6.2	69.600°	1.42007	1.4201
Glucose ($C_w = 50\%$)	69.340°	−0.130°	4.9	4.8	69.381°	1.41804	1.4181

Note. 1. C_w: wt% concentration; 2. $[\alpha_s] = 44.8$ for glucose at 632.8 nm; $[\alpha_s] = 55.85$ for saccharose at 632.8 nm, which is obtained with curve-fitting technique.

from [7,14]) and L the optical path length of the chiral liquid. Table 1 lists essential experimental and calculated parameters of the two chiral samples, together with the $[\alpha_s]$ values from [7,14] for reference. From Fig. 3, it is obvious that the value $|\phi|$ changes abruptly as θ increases to approach θ_c.

4. Measurement resolution of the method

If the conditions $\theta = \alpha = 45°$ are chosen as that used in the general polarization interferometer, then $|\phi|$ is in the range 0–0.001° as $\theta < \theta_c$. ϕ thus is too small to be detected with a commercial high-resolution phase meter. In our experiments, we have achieved the measurement of $|\phi|$ to be about 0.1–0.2°. It is obvious that the value of $|\phi|$ has been enhanced from 2 to 4 orders of magnitude. While $\theta > \theta_c$ in our experimental conditions, ϕ occurs due to the total internal reflection and it is independent of the chiral parameter. Under this condition the average refractive index can be estimated from the data of ϕ, as reported in [10].

From Eq. (16) we get

$$\Delta n = |n_0 \cos\theta_c| \cdot \Delta\theta, \tag{18}$$

where Δn and $\Delta\theta$ are the uncertainties in n and θ, respectively. Substituting the angular resolution $\Delta\theta = 0.001°$ of the rotation stage and θ_c into Eq. (18), we have $\Delta n \cong 1 \times 10^{-5}$ for both two tested solutions in our experiments.

Under our experimental conditions, Eq. (15) can be simplified as

$$g \cong -\frac{n_0 q_1(\cos\theta + q_1)\left[(n/n_0)^2\cos\theta - q_1\right]\phi}{2\sin^2\theta\cos\theta\tan\alpha}. \tag{19}$$

So we have

$$\Delta g = \left|\frac{dg}{d\phi}\cdot\Delta\phi\right| + \left|\left(\frac{dg}{dq_1}\cdot\frac{dq_1}{d\theta} + \frac{dg}{d\theta}\right)\Delta\theta\right| + \left|\left(\frac{dg}{dq_1}\cdot\frac{dq_1}{dn} + \frac{dg}{dn}\right)\cdot\Delta n\right|, \tag{20}$$

where Δg, $\Delta\phi$, $\Delta\theta$ and Δn are the uncertainties in g, ϕ, θ and n, respectively. Considering the second harmonic uncertainties and the polarization-mixing uncertainties, the total phase difference uncertainty $\Delta\phi$ can decrease to 0.002° in our experiments [11]. Substituting these data, $\Delta\theta = 0.001°, \Delta n \cong 1 \times 10^{-5}, \alpha = 88°,\ n_0 = 1.51509,$ the estimated values of n and g into Eq. (20), we can depict the relation curve of Δg versus θ, as shown in Fig. 4. As θ approaches θ_c, the last two terms in Eq. (20) approach infinite and Δg changes abruptly. This fact can be seen that Δg in Fig. 4. Both of them have the same resolution $\Delta g \cong 2 \times 10^{-8}$ as θ is in the ranges of 69.3–69.35° and 69.45–69.55°, respectively.

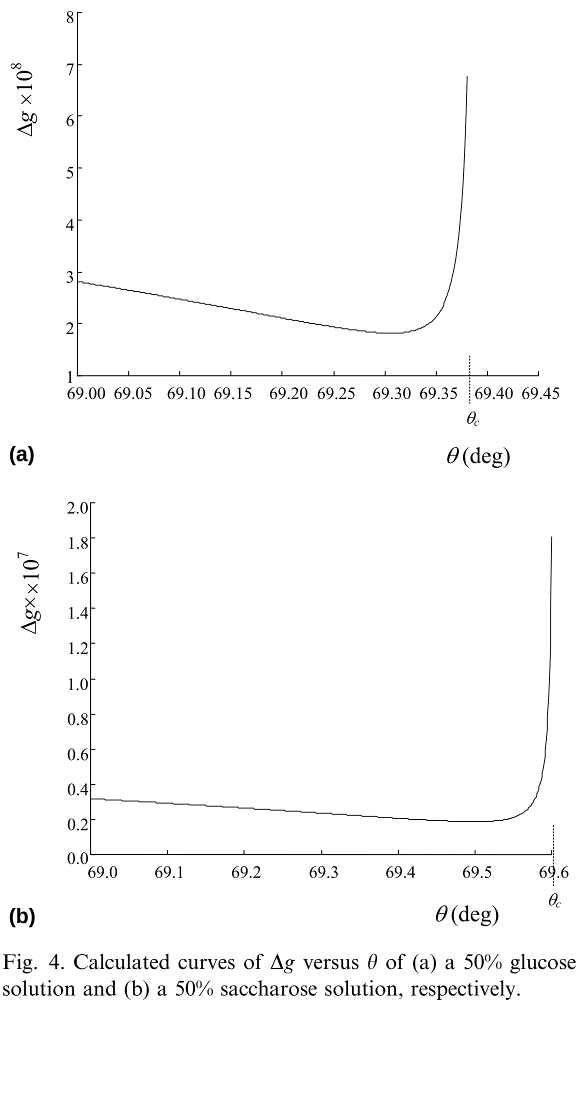


Fig. 4. Calculated curves of Δg versus θ of (a) a 50% glucose solution and (b) a 50% saccharose solution, respectively.

5. Conclusion

We have here presented an alternative method for measuring the chiral parameter and the average refractive index of a chiral liquid using only one set of optical configuration. The phase difference between s- and p-polarizations of the reflected light is enhanced and measured under appropriate conditions. Because of the experiment common-path configuration and heterodyne phase measurement, it has such merits as high stability and high resolution. We measured both 50% glucose solution and 50% saccharose solution with an accuracy of 1×10^{-5} for the average refractive index and 2×10^{-8} for the chiral parameter, respectively.

Acknowledgements

This study was supported in part by National Science Council, Taiwan, ROC, under contract NO. NSC 90-2215-E-009-077.

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