

Direct Phase Measurement of Optical Rotatory Dispersion

Honors Project

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By

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## List of Symbols

$\lambda$ , wavelength (nm)

$f$ , frequency ( $\text{s}^{-1}$ )

$c$ , speed of light ( $3.08 \times 10^8 \text{ m s}^{-1}$ )

$\theta$ , optical rotation (degrees)

$[\alpha]$ , specific rotation ( $^{\circ} \text{ dm}^{-1} (\text{g/mL})^{-1}$ )

$C$ , concentration (g/mL)

$l$ , path length (dm)

$A$ , rotation constant ( $2.17 \times 10^7 \text{ deg nm}^2 \text{ mL dm}^{-1} \text{ g}^{-1}$ ) per Mahurin *et al*

$\lambda_0$ , dispersion constant (131 nm) per Mahurin *et al*

## ABSTRACT

### DIRECT PHASE MEASUREMENT OF OPTICAL ROTATORY DISPERSION

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Recent advances in photon detection provide cutting-edge optical measurements that are accessible to undergraduate physics and chemistry labs. Furthermore, the advent of affordable auto-balanced photoreceivers increases the likelihood of shot noise limited measurements becoming a reality. However, minor obstacles must be overcome before there is implementation of relatively rigorous training and research that would involve such measurements. First, the measurement theory pertaining to an appropriate experiment should be relatively transparent. Second, instrumentation issues based on fundamental principles of optics should be realized through simpler, yet similar, experiments. This work provides sufficient background to help overcome both of these hurdles. Essentially, some key foundational aspects of dual beam photometry are addressed utilizing a previously designed crossed-beam spectropolarimeter. The instrument was assembled and evaluated utilizing the optical rotatory dispersion (ORD) of sucrose.

## **I. Background**

### *1.1 Polarized light: Formation and Measurement*

Polarized light is often depicted as a transverse wave comprised of oscillating electric and magnetic fields oriented perpendicular to one another (see Fig. 1). In addition to their mutual perpendicular directions, these fields also oscillate in directions that are perpendicular to the propagation direction (i.e. the direction the light travels). The polarization direction of light indicates the direction of the electric field oscillation. The number of times the electric field changes polarity per second is the frequency (i.e. color of the light). Polarized light serves as a valuable tool to many areas of science, e.g. chemistry as valence shell electrons of atoms respond to the electric field.

Linearly polarized light defines a type of polarization in which the electric field is constrained to oscillate in a fixed plane and it may be used as a probe to gain information about the structure of materials. Specifically, we set out to develop a spectropolarimeter (see section 1.2 below) that measures the amount of rotation a transparent, chiral solution induces in polarized light at different frequencies (colors), a phenomenon called optical rotatory dispersion. A wide variety of commercially available spectropolarimeters, of varying sophistication and cost are already available.<sup>1</sup> However, in recognizing the pedagogical value of an earlier design<sup>1</sup> we were motivated to build a similar version of this low cost instrument.

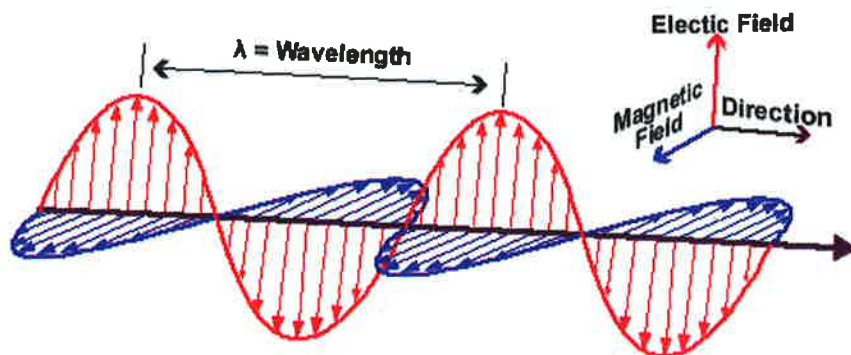
Furthermore, such experimental methodology serves as a design platform for a more sophisticated, and more sensitive, measurement technique based on auto-balanced detection.

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<sup>1</sup> (e.g.) JASCO J-815, JASCO J-1500, DSM 1000 Spectrophotometer



The latter can be coupled with phase-sensitive detection to provide the highest sensitivity per cost ratio utilizing current technology.



**Figure 1.** Light wave (source: photonics.com)

There are four ways to constrain the orientation of the electric field in a plane and hence produce linearly polarized light. They include polarization via Rayleigh, or molecular scattering, reflection at Brewster's angle (macroscopic scattering), birefringent crystals (i.e. crystals having two optical axes with differing refractive indices), and selective absorption, typically using doped polymer films manufactured in such a manner as to absorb all electric fields not in a particular direction. Of the four methods used to create polarized light, the crossed-beam spectropolarimeter relied on selective absorption by utilizing polaroid films. Although birefringent crystals provide the best method of polarization due to their relatively high extinction coefficients<sup>ii</sup> (i.e. polarization "purity") and are therefore used in most laboratory

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<sup>ii</sup> For more information: [Olympus Microscopy Resource Center](#)

instruments, they are somewhat expensive and require beam alignment not as well suited to the methodology exploited in our apparatus. In contrast, the relatively thin polaroid films are more advantageous in this "crossed-beam" spectropolarimeter design, as they are more immune to the deleterious effects of beam crossing geometry.

### *1.2 Spectropolarimetry*

Measuring the effects of materials on the polarization of light affords complementary information that is not available from ordinary intensity spectra (i.e. absorption measurements). For example, an intensity spectrum, a scalar value, can be used to determine the concentration of the molecules in solution based on the linear relationship between absorbance and concentration as defined by the Beer-Lambert Law; whereas, the physical mechanisms causing polarization changes are different from those responsible for the features related to intensity spectra. In contrast to intensity spectrum, the polarized spectrum enables the determination of vector quantities, e.g. the electric and magnetic field vectors, thus allowing spectropolarimetry to expand our view into the nature of materials. For example, polarization analysis helps provide information concerning the structure and orientation of molecules, both of which are helpful in establishing the identity, and potential applications, of materials.

Essentially, spectropolarimetry involves the measurement and subsequent analysis of the polarization of light at various wavelengths,  $\lambda$ , or alternatively, at various frequencies,  $f$  (since the speed of light,  $c$ , can be written as  $c = f\lambda$ ). Specific optically active solutions produce a characteristic rotation of the polarization at a given wavelength. For example, when subjected to a light source (i.e. a polarized "probe") a chiral compound can be identified based on the resulting polarization rotation of optically active species in concentration (see section 1.3 below).

Of particular interest to the author, spectropolarimetry is invaluable to chemists wishing to differentiate between enantiomers, chiral molecules that are non-superimposable mirror images of each other, based on their differences in polarization rotation. Because spectropolarimetry can be used to determine the identity and structure of chiral molecules, technologies that make such measurements with ever-increasing precision are invaluable to the designers and manufacturers of pharmaceuticals.

### 1.3 Optical rotation

In solution, chiral molecules have the ability to rotate the plane of polarized light. This effect is known as optical rotation. Optical rotation ( $\theta$ ) of an optically active solution is expressed as:

$$\theta = [\alpha]Cl \quad (1)$$

where  $[\alpha]$  is the specific rotation of the optically active solution,  $C$  is the concentration of the solution in grams per milliliter, and  $l$  is the path length the light travels through in the sample. Specific rotation is a function of sample temperature and the wavelength of the light used to probe the sample

To evaluate the effectiveness of our CBS, the wavelength dependence of the specific rotation, a phenomenon known as optical rotatory dispersion, of a known compound, sucrose, was utilized. Optical rotatory dispersion (ORD) is the change in optical rotation of linearly polarized light as a function of wavelength. Specifically, it describes the indirect relationship between optical rotation and wavelength. For most materials, increasing the wavelength of the light decreases the ability of the chiral sample to rotate light.

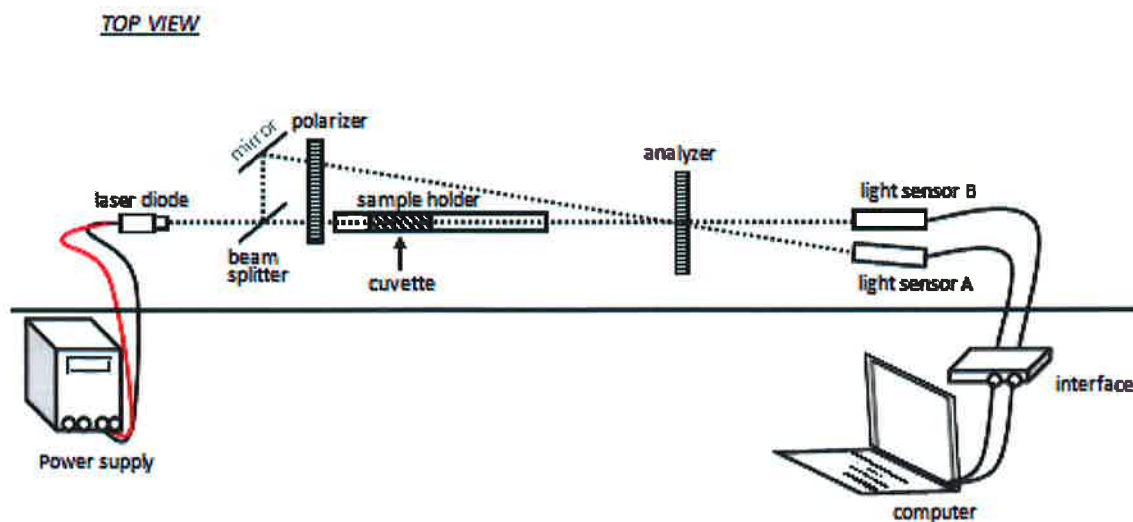
## II. Materials and Method

### 2.1 Description of Apparatus: Crossed-beam Spectropolarimeter

The crossed-beam spectropolarimeter (CBS), similar to that designed by Kraftmakher<sup>1</sup>, is shown in Fig. 2. Laser diodes with wavelengths of 633nm and 513nm, respectively, were chosen for this investigation. The laser beam was incident on a 50% beam splitter (Hewlett Packard 10701A) in which 50% of the laser beam was transmitted and 50% of the laser beam reflected. This particular beam splitter was used as it was readily available in our laboratory. However, it was specifically designed, utilizing an anti-reflective coating, for use with a HeNe gas laser with a wavelength of 633nm. So, the beam splitter was ideal for the 633nm diode laser. In addition, we also managed to effectively use the beam splitter for the green diode laser (514nm) by careful positioning a suitable beam aperture to eliminate unwanted surface reflections.

The transmitted beam (i.e. the signal) was directed through the chiral sample while the reflected beam (i.e. the reference) was diverted using a front surfaced mirror. An inexpensive thin film polarizer was positioned just after the beam splitter and reference mirror and prior to the sample. Such placement ensures that the polarization of the reference and signal beams are in phase. That is, the plane of the electric fields for the signal and reference beams coincide. The front surfaced mirror was housed in an adjustable mount, which allowed the reference beam to be positioned and facilitate a precise overlap with the signal beam in the analyzer (i.e. polarizer). The analyzer was mounted so that it could be manually rotated without blocking either laser beam while acquiring data. The two laser beams were carefully aligned to ensure intersection in the second polarizer (i.e. the analyzer) which maximized the uniformity of the overlapping beam geometry – hence, crossed-beam spectropolarimeter.

A 10 cm polarimeter tube containing the chiral solution (i.e. the sample) was positioned in the signal path between the polarizer and analyzer. A chiral solution imposes a rotation in the polarization direction of the signal beam that passes through it. The polarized reference beam maintains the incident polarization direction since it does not pass through the sample. Finally, two light sensors (PASCO CI-6504A) were situated to simultaneously monitor the reference and signal beams. A Science Workshop 750 PC interface was used to power the light sensors and acquire the light intensity measurements. Data Studio software was used for real time data display and storage for subsequent analysis using MS EXCEL. In this manner a graph of the signal vs. reference will produce an ellipse, the shape of which allows the determination of the phase shift, which is twice the optical rotation.



**Figure 2.** Diagram of crossed-beam spectropolarimeter.

## 2.2 Reagents and solutions

All solutions were prepared just prior to analysis using distilled dionized water. The sucrose (CAS 57-50-1): certified A.C.S. was aquired from Fisher Scientific. The distilled dionized water was filtered prior use in solution preparation to remove particulates (i.e. dust and lint) that were present in the water from the storage container/glassware.

## 2.3 Measurment of rotation angle

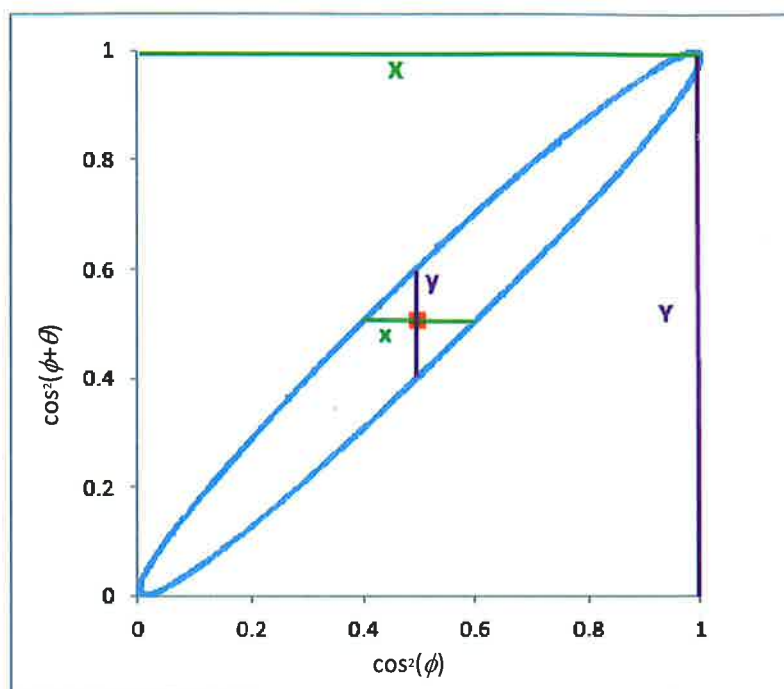
To acquire data with or without the sample present, the analyzer was manually rotated. The reference beam intensity is proportional to  $\cos^2(\phi)$  while the signal beam is proportional to  $\cos^2(\phi + \theta)$ , where  $\phi$  is the relative angle between the polarizer and analyzer and  $\theta$  is the polarization rotation induced by a chiral sample (Fig. 3). If water (an achiral liquid) is used then  $\theta = 0^\circ$ . Using trigonometric identity,  $\cos^2 \phi = \frac{1}{2} (1 + \cos 2\phi)$  it follows that the optical rotaiton is one half the phase shift between the signal and reference. The shape of the ellipse determines the optical rotation according to either of the relations<sup>1</sup>:

$$\theta = \frac{1}{2} \sin^{-1} (x/X) \quad \text{or} \quad \theta = \frac{1}{2} \sin^{-1} (y/Y) \quad (2)$$

where the values for x, X and y, Y are depicted in Fig. 2. We used the average of the two optical rotation relations as the reported value. The percent difference between the two can be used to estimate errors.

When the data set is normalized, X and Y are equal to 1 (as shown in Fig. 3.) The normalization of data simplifies the relations and so the experimentally computed optical rotation becomes for each data run.

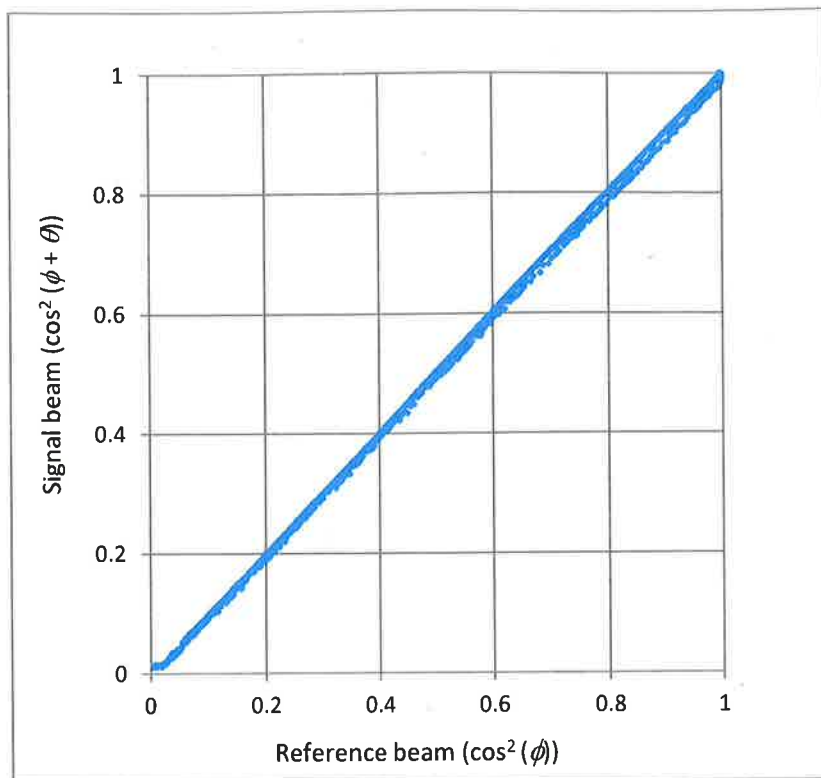
$$\theta = \frac{1}{4} (\sin^{-1}(x) + \sin^{-1}(y)) \quad (3)$$



**Figure 3.** Graphical representation of optical rotation:  $\cos^2(\phi + \theta)$  vs.  $\cos^2(\phi)$

The signal beam entered the polarizer and analyzer near the ideal incidence angle of  $0^\circ$ , meaning it was orthogonal to the surface of the polaroid films, whereas the reference beam entered the polarizer and analyzer at approximately  $5^\circ$  degrees. This small angle is acceptable provided the scope of this experiment and is essential to allow the polarizers to function

adequately.<sup>2</sup> The confirmation of an “acceptable optical layout” followed from the acquisition of a straight line (no indication of ellipticity with  $\theta = 0^\circ$ ) in the graph of signal vs. reference (see Fig. 4) as the analyzer was rotated utilizing the achiral water sample only.



**Figure 4.** Signal vs. Reference- water sample.



### III. Results and Discussion

The optical rotation of sucrose solutions was experimentally determined in the newly assembled CBS using diode lasers with wavelengths,  $\lambda = 633$  nm (Fig. 5.1) and  $\lambda = 513$  nm (Fig. 5.2). Utilizing the set of ellipses in Fig 5.1 and Fig 5.2 and eqn. 3, we find:

633 nm		514 nm	
$C$ (g/mL)	$\theta$ (°)	$C$ (g/mL)	$\theta$ (°)
0.03	2.0	0.06	5.8
0.06	3.2	0.09	8.5
0.15	8.5	0.15	14.0
0.18	10.1	0.18	16.2

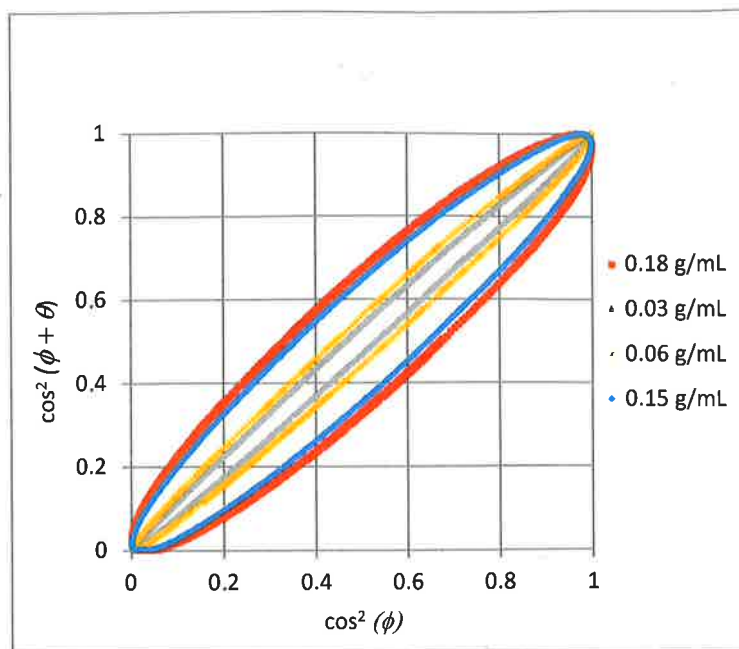
**Table 1.** Experimental data at 633 nm and 514 nm.

The linear regression equation of the measured optical rotation vs. sucrose concentration for the CBS at these wavelengths (Fig. 6) was

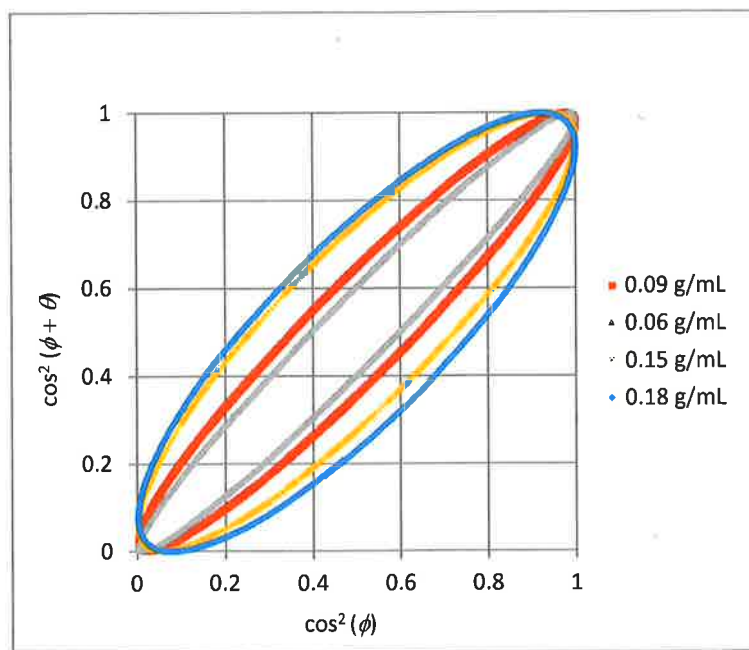
$$633\text{nm} : \theta_{\text{sucr}} = 55.8 * C_{\text{sucr}} + 0.1088; R^2 = 0.9977 \text{ where } [\alpha] = 55.8 (^\circ \text{ dm}^{-1} (\text{g/mL})^{-1})$$

$$514\text{nm} : \theta_{\text{sucr}} = 87.2 * C_{\text{sucr}} + 0.6584; R^2 = 0.9983 \text{ where } [\alpha] = 87.2 (^\circ \text{ dm}^{-1} (\text{g/mL})^{-1})$$

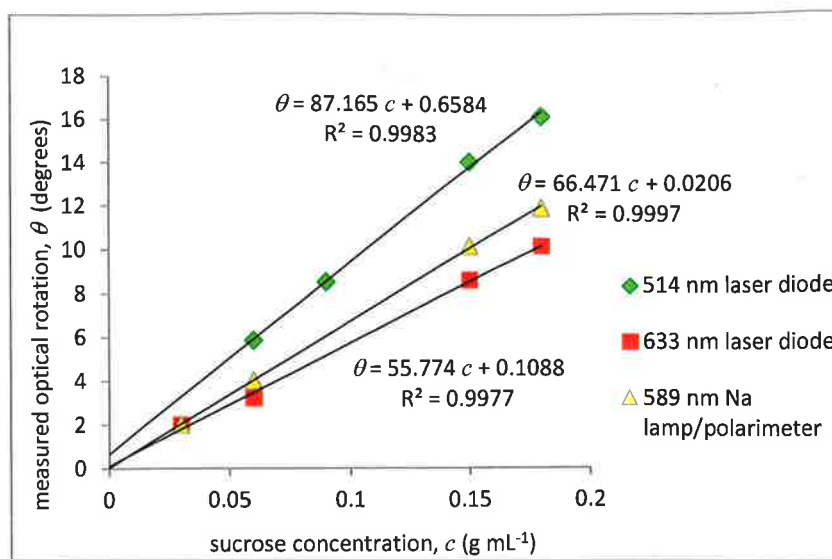
respectively.



**Figure 5.1** Optical rotation of sucrose solutions at 633 nm.



**Figure 5.2** Optical rotation of sucrose solutions at 514 nm.

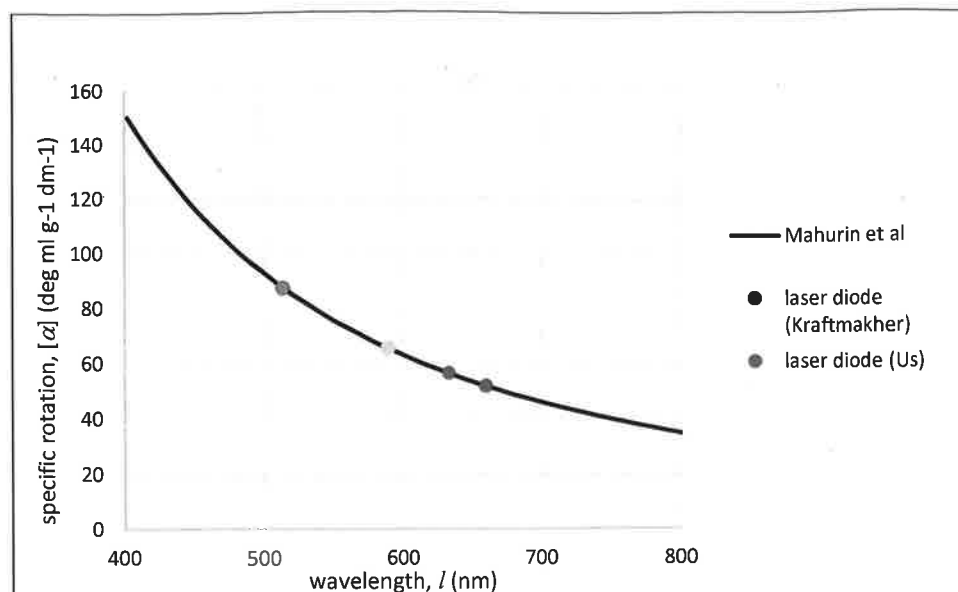


**Figure 6.** Measured optical rotation vs. sucrose concentration at various wavelengths.

In previous experiment<sup>3</sup>, the wavelength dependence (i.e. dispersion) of the specific rotation of sucrose was obtained via the Drude expression:

$$[\alpha] = A / (\lambda^2 - \lambda_0^2) \quad (4)$$

where the rotation constant,  $A$  is  $2.17 \times 10^7 \text{ deg nm}^2 \text{ mL dm}^{-1} \text{ g}^{-1}$ , the dispersion constant,  $\lambda_0$  is 131 nm, and  $\lambda$  is the wavelength of the light source in nm. We utilized the Drude expression and constants to generate an expected optical rotatory dispersion curve (Fig. 7). Those  $[\alpha]$  values were then compared to the experimental ones obtained from the slope of the line of best fit for  $\theta$  vs.  $C$  at each wavelength to determine percent error (Table 2).



**Figure 7.** Optical rotatory dispersion curve for sucrose--- compilation of previous results with our collection of data

$\lambda$ (nm)	calculated $[\alpha]$	experimental $[\alpha]$	Percent error (%)
514	87.8	87.2	0.73
589	65.8	66.5	1.06
589	66.6*	66.5	0.15
633	56.6	55.8	1.38

**Table 2.** Percent error values for experiment -\*  $[\alpha]$  provided by sucrose manufacturer.

The  $[\alpha]$  values obtained at 589 nm were determined using a fixed  $\lambda$  a polarimeter (LINOS Photonics SR6). The manufacturer of the sucrose used in this experiment cites the  $[\alpha]$  of its product as 66.6 ° whereas the Drude equation yields a value of 65.8 °. While there is an average approximate error of 1% in the CBS, it is likely this error is higher than the actual error due to the slight inaccuracy of the calculated  $[\alpha]$  obtained from the above determined values (i.e. rotation and dispersion constant) utilizing the Drude equation.

### *3.1 Instrumentation design considerations and potential improvements*

The development of the CBS revealed several technical difficulties, where minimizing such is key to proper functioning of the apparatus (e.g. the overlap geometry at the cross sectional areas of the beams at the analyzer). To prevent the beams from straying over the active area of the analyzer as it rotated, the signal and reference beams were aligned to intersect as near to the rotation center of the analyzer as possible. Another subtle issue involved laser beam focusing. When the laser beams were too focused (produced a small dot) both saturation effects (i.e. too many photons for the analyzer to absorb as it is rotated) and poor beam overlap occurred. In contrast, a large beam size exposed inhomogeneities in the polarizer that were amplified in such a way that can lead to undesirable deviations in the data. Therefore, a balance between photon number density and inhomogeneities in the polaroid film must be achieved in order to obtain quality measurements. Replacing the low quality polaroid film with a high quality film polarizer (e.g. a nanowire polarizer<sup>iii</sup>) will mitigate such issues significantly. Strategic placement of beam apertures are also helpful to maintain proper alignment and reproducibility.

Furthermore, issues involving laser polarization and “laser output drift” (i.e noise) were somewhat minimized via an additional polarizer, either in the signal or reference beam path, and a regulated power supply. Some types of diode lasers emit partially polarized light that result in significant intensity differences in the signal and reference beam. The use of the additional polarizer will ensure the intensities of both beams were nearly equal. Also, because the laser intensity (i.e the number of photons the diode laser emits) depends on diode temperature and

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<sup>iii</sup> [Nanoparticle Linear Film Polarizers](#)

current, fluctuations in laser output can be reduced using both laser diode current and temperature controllers.

Beam scattering at the light sensor detector entrance, on occasion, translates into poor signal quality and skew the data. Fiber optic pick-ups can be coupled to the detectors to minimize these effects. For high precision work it is advisable to replace the manual rotation mount with a motorized rotation mount<sup>iv</sup> with an additional small aperture glued to the center of the analyzer.

#### **IV. Conclusion**

The experimentally determined values of the specific rotation of sucrose proved the CBS to be a relatively straightforward and accurate method of measuring the specific rotation for concentrations of sucrose ( $0.03 - 0.18 \text{ g mL}^{-1}$ ). Additionally, this work highlights the dependence of specific rotation (i.e. specific rotation decreases with increasing wavelength) and provides a solid foundation for the experimental background needed to develop a more precise spectropolarimeter based on auto-balanced photodetection.

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<sup>iv</sup> [Motorized Precision Rotation Mount](#)

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