

## Demonstration of Optical Rotatory Dispersion of Sucrose

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Molecules whose mirror images are nonsuperimposable are called chiral (Greek for handed) and they exhibit optical activity. Optical activity is observed as circular dichroism, the difference in extinction for right- and left-circularly polarized light passing through the medium, or optical rotation, the rotation of the plane of polarization of linearly polarized light passing through the medium. Because linearly polarized light is a coherent superposition of right- and left-circularly polarized light, the two phenomena are related. Formally, circular dichroism and optical rotation are related through the Kramers–Kronig relations (1); knowledge of the complete spectrum of one allows the calculation of the other. The optical rotation angle,  $\varphi$  (in radians), is often written as (2)

$$\varphi = \frac{\pi(n_L - n_R)\ell}{\lambda} \quad (1)$$

where  $n_L - n_R$  is the difference in the indices of refraction for left- and right-circularly polarized light of the optically active medium at a wavelength  $\lambda$ , and  $\ell$  is the path length.

The precise angle through which the linearly polarized light vector is rotated for a given chiral medium is determined by the density or concentration of the optically active component, the path length, the wavelength, and the temperature. The specific rotation has been adopted as a useful quantitative measure of these effects. The specific rotation for a chiral solution of a chiral compound, denoted by  $[\alpha]_{\lambda}^T$ , is defined as

$$[\alpha]_{\lambda}^T = \frac{\theta}{\ell c} \quad (2)$$

in units of  $\text{deg dm}^{-1} \text{g}^{-1} \text{mL}$  where  $\theta$  is the measured angle of rotation (in deg),  $\ell$  is the distance (in dm) of the optically active solution through which the light travels, and  $c$  is the concentration (in  $\text{g mL}^{-1}$ ). To standardize the reporting of specific rotation, values are typically given at room temperature using the sodium D line (with a wavelength of 589 nm). A plot of the specific rotation of a chiral medium as a function of wavelength is called an optical rotatory dispersion curve and it can be useful for gaining insight into the electronic structure of the medium of interest. For wavelengths that are well outside a single resonance absorption region of the material, the optical rotatory dispersion can be described by the Drude expression (3):

$$[\alpha]_{\lambda}^T = \frac{A}{\lambda^2 - \lambda_0^2} \quad (3)$$

where  $A$  is called the rotation constant and  $\lambda_0$  the dispersion constant. If several optically allowed transitions contribute in the region of wavelength  $\lambda$ , the optical rotation is a sum over such expressions. When the specific rotation of a compound decreases with increasing wavelength as in eq 3 and there are no local extrema in the curve, the optical rotatory dispersion (ORD) curve is called a plain curve.

Many articles have appeared describing demonstrations of optical rotation (4–15). In this paper, we describe a particularly vivid demonstration of optical rotation, which can be easily instituted in the undergraduate chemistry or physics laboratory. Recently Zare et al. (16) presented a simple method for detecting the optical activity of a chiral medium by directly observing the rotation of the plane of polarization of light as it propagates through an optically active solution. Linearly polarized light from a HeNe laser is directed down a 1-m cylindrical glass tube filled with a solution containing chiral molecules. Polarized light is scattered at right angles to the direction of propagation as a result of a combination of Tyndall and Rayleigh scattering. Maximum scattering intensity occurs at right angles to the plane of polarization. The rotation of the beam is clearly seen as alternating bright and dark regions as the light polarization vector “spirals” along the tube. In this study, we extended this method of observing the optical activity of a chiral medium to include the calculation of the specific rotation and extinction coefficient. In addition, we used various wavelengths (456.9, 476.5, 488.0, 514.5 nm) supplied by an argon ion laser, the 632.4-nm line from a HeNe laser, and the 785 nm line from a diode laser to create the ORD and extinction curves for sucrose in water. The ORD curve was used to fit the Drude expression (eq 3) and to obtain values for the rotation and dispersion constants.

### Experimental Procedure

The experimental setup is shown in Figure 1. Either a helium–neon, an argon-ion, or a diode laser was used as the light source in these experiments. Because the scattered light was detected with a photomultiplier, the intensity of the laser beam was not a major consideration. As a result, the laser can be operated at a relatively low output power. The partially

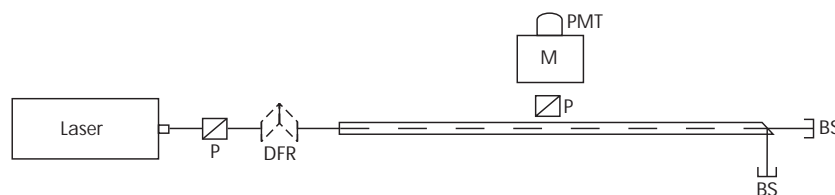


Figure 1. The experimental setup. A beam from the laser (HeNe or argon ion) is linearly polarized (vertically in the figure) by a Glan-air prism (P) before entering the cell. A double Fresnel rhomb (DFR) can be used to rotate the polarization vector in order to observe the movement of the bands. The second linear polarizer is placed between the cell and the monochromator (M) and the photomultiplier tube (PMT).

polarized laser beam was further polarized with a glan-air prism or polarizer sheet in order to ensure maximum linear polarization. If the output of the laser system is nearly linearly polarized, this polarizer feature may not be necessary, particularly for simple demonstrations.

To demonstrate the effect, corn syrup (e.g., Karo syrup) is ideal; however, corn syrup is a complex mixture of sugars and polysaccharides. To make quantitative measurements, a sucrose solution was used with a concentration of 0.81 g/mL (made by dissolving 81 g of sucrose in enough water to make 100 mL of total solution). It is important that the sugar be completely dissolved in the water and that the solution be homogeneous throughout. Inhomogeneity in the solution results in a bending of the laser beam due to changes in the index of refraction as the beam travels along the length of the tube. Microscope slides were attached with epoxy to the ends of a 120-cm Pyrex tube with a diameter of 2 cm. The entrance window was perpendicular to the tube axis and the exit window was attached at an angle of approximately  $60^\circ$  to minimize backscattering of the laser beam. For safety, the exit window was positioned to direct the reflected laser beam down toward a beam stop, as shown in Figure 1.

The detector system consisted of a second linear polarizer whose polarization axis was perpendicular to the direction of laser propagation and parallel to the polarization of the incident laser beam. A monochromator equipped with a photomultiplier tube was used to measure the intensity of the scattered beam. Alignment of the detector along the beam was important. The detector must be at the same height as the beam and at the same distance from the beam to ensure that no errors in the measured intensity were incurred. To

obtain the specific rotation of the sucrose, the detector was mounted on a track and moved along the length of the tube in intervals of 1.0 cm. The intensity of the scattered beam was recorded as a function of distance. It is also possible to keep the detector fixed and to use a light pipe in which one end can be moved down the tube while the other end is attached to the monochromator. No measurements were taken near either end of the tube because of the small amount of scattering at the entrance and exit windows.

## Results

Figure 2 shows photographs of the demonstrated effect. For the 785-nm line produced by the diode laser it is necessary to use an infrared viewer and therefore this feature is not shown. For demonstration purposes, it is interesting to configure the tube vertically and to walk around it watching the right-hand rotation of the light vector (for sucrose). Also, if one uses a double Fresnel rhomb to rotate the polarization clockwise, the bright bands are seen to advance outward along the laser beam direction. In contrast, fructose, whose specific rotation is negative, requires a counterclockwise rotation of the polarization in order for an advance of the bright bands to be seen. This characteristic can be used to determine the sign of the specific rotation. In addition, the "invert" sugar reaction can be performed. This involves introducing concentrated HCl into the tube of sucrose solution. The acid breaks the sucrose down into glucose and fructose, causing a change in the optical rotation of the solution that can easily be measured. All these observations make for a very effective lecture demonstration of optical rotation with the HeNe laser. A plot



Figure 2. A photograph of the optical rotation of laser light as it propagates through a sucrose solution. The wavelengths seen here are 632 nm (from a HeNe laser), 514 nm, 488 nm, and 457 nm (from an argon ion laser).

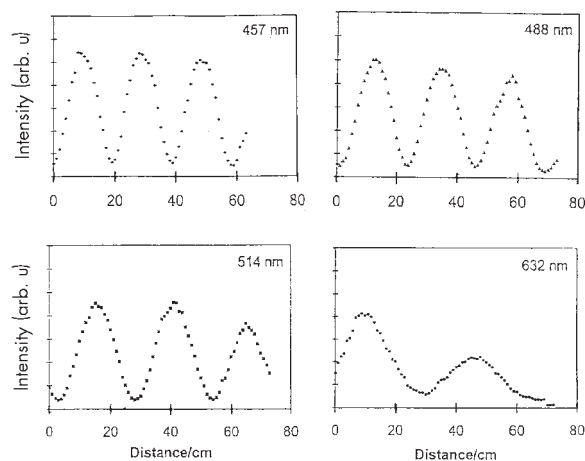


Figure 3. Measurements of the scattered light intensity as a function of path length for various wavelengths of linearly polarized laser light propagating through a sucrose solution (0.81 g/mL).

of intensity versus distance,  $x$ , exhibited a  $\cos^2 x$  distribution as shown in Figure 3 for all wavelengths used. The initial position was taken to be approximately 10 cm from the end of the tube. In principle, it is possible to determine the specific rotation from any two points on these curves. In this work,  $[\alpha]_{\lambda}^T$  was determined, however, from the distance between maximum or minimum intensities. The distance between consecutive extrema,  $L$ , corresponds to a polarization rotation of  $\pi$ . The specific rotation is then equal to  $\pi/Lc$ , or  $180^\circ/Lc$ .

Using this method, a very accurate specific rotation can be determined from the average of a large number of measurements. For demonstration purposes, it is possible to use a meter stick and the unaided eye to determine the distance between bright or dark spots and thus to estimate the specific rotation.

The ORD curve and its fit to eq 3 are shown in Figure 4. The fitted curve was obtained using a nonlinear iterative fitting method. By inputting initial parameters that minimize  $\chi^2$  (which is a goodness-of-fit parameter), the values of the rotation and dispersion constants were found to be  $A = 2.17 \pm 0.02 \times 10^7 \text{ deg nm}^2 \text{ dm}^{-1} \text{ g}^{-1} \text{ mL}$  and  $\lambda_0 = 131 \pm 10 \text{ nm}$ . These values are in agreement with the values of  $A = 2.1648 \times 10^7 \text{ deg nm}^2 \text{ dm}^{-1} \text{ g}^{-1} \text{ mL}$  and  $146 \text{ nm}$  (17). One could also plot  $1/[\alpha]_{\lambda}^T$  vs  $\lambda^2$  and perform a linear least squares fit to obtain the two constants. The precision of the ORD measurements could be greatly improved by using a tunable laser.

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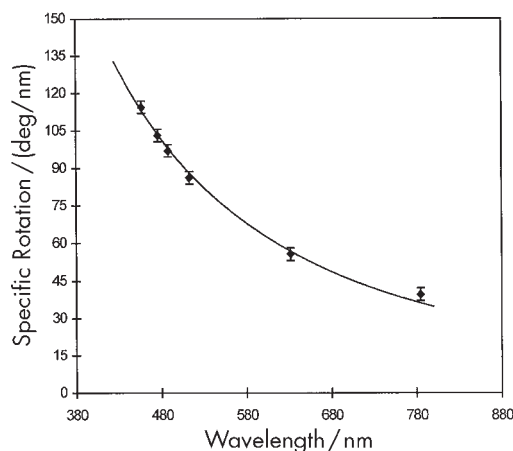


Figure 4. The optical rotatory dispersion curve measured for sucrose in water, compared with the Drude expression (eq 3).

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