Using Guided Inquiry to Study Optical Activity and Optical Rotatory Dispersion in a Cross-Disciplinary Chemistry Lab

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General Concept

Optical activity and optical rotatory dispersion (ORD) are important topics in many areas of chemistry including organic (1) and physical (2) chemistry and biochemistry (3) and have found their way even into general chemistry textbooks (e.g., ref 4). As one recalls, an optically active substance is a substance that rotates the plane of polarization of plane-polarized light. We can define the specific rotation, [α], of an optically active substance as follows:

$$[\alpha] \equiv \alpha/(\ell \times c) \qquad (1)$$

where α is the temperature- and wavelength-dependent angle of optical rotation by the sample, ℓ is the length of the sample tube in units of decimeters, and c is the concentration in units of grams of solute per cubic centimeter of solution (1).

Determination of specific rotation using a polarimeter is a standard part of an organic chemistry lab curriculum. What remains outside the scope of such a lab is the phenomenon of ORD, which is the variation of optical activity of a given sample with the wavelength λ of light (1, 2). Qualitative correlations can be used to relate the sign of the slope of the [α](λ)-dependency (called ORD curve [5]) to the absolute stereochemistry of molecules with similar structure. As an example, the ORD curves of a number of cyclic ketones have been studied as model systems in order to establish a relationship between three-dimensional molecular structure and the corresponding ORD curve. As a result, an empirical set of rules, known as the octant rule, has been developed allowing one to predict the absolute stereochemistry of a cyclic ketone on the basis of the sign of its dispersion curve (5). A quantitative description of ORD is provided by Drude's equation (6):

$$[\alpha] = C/(\lambda^2 - \lambda_0^2) \qquad (2)$$

where C is a constant, and λ_0 is the wavelength of the closest absorption maximum (about 210 nm for carvone). Sometimes, a modified version of Drude's equation is used (6):

$$[\alpha] = C_2/\lambda^2 \qquad (3)$$

Studying ORD by a common polarimeter alone is impossible because the wavelength of its light source (D-line of a sodium vapor lamp, λ = 589 nm [1]) is fixed. We therefore designed an extended version of the optical-activity lab in which an inexpensive He–Ne laser (λ = 633 nm) serves as a light source at a wavelength different from the D-line of sodium.

Prior to the lab, students are given a half-hour mini-lecture on the effects to be studied (polarization, optical activity, and ORD). Before beginning the main part of the lab, they determine the angle α_2 of optical rotation of S-(+)-carvone for λ = 589 nm using a common polarimeter; it turns out that $\alpha_2 = 56.1°$. For the main part of the lab, they are provided with a laser mounted in standard fashion on an optical rail or bench, a pair of polarizers[1] in holders (one of them rotating and
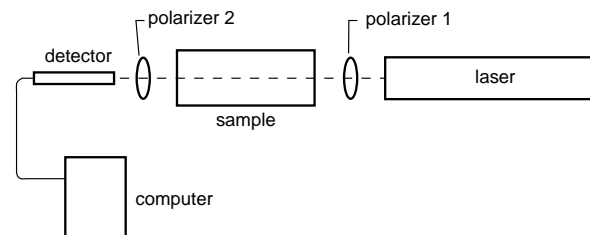

Figure 1. Setup for the laser-based studies of optical activity.

provided with a scale in degrees), a simple light-intensity detection system, the optically active sample (S-(+)-carvone), and a sample holder, and are challenged to use this equipment to develop the most accurate method for determination of the angle of optical rotation, α, at λ = 633 nm. Their ultimate goal is to determine which equations, the Drude equation or its modified version, better describes the data they are about to obtain.

Of course, the main challenge of the experiment is to figure out how to accurately determine the direction of polarization of light at the entrance to polarizer 2 (see Fig. 1) *before* and *after* the sample is inserted in the optical path. The difference will indicate the magnitude of α. The remainder of this paper describes three possible approaches to solving this problem, through which the students are guided.

Measuring the Optical Activity with the Laser Setup

Our approach in conducting this portion of the lab is guided inquiry, a method that has recently been implemented successfully in another physical chemistry laboratory course (7). The class is divided into groups of three students each. After a 30-minute mini-lecture on optical activity and ORD, the students have the background needed for the guided collaborative work. The first assignment the students are given is to assemble the experimental setup that would allow them to find the direction of polarization of the laser beam (they should come up with a setup similar to that shown in Figure 1 on their own). What follows is well summarized in ref 7: "Students may think they know the answer before beginning, but are soon forced to face a misconception and reconcile their data with their flawed intuition." In our case, they see it as natural to find the direction of polarization by rotating the circular holder (where polarizer 2 is mounted) until the light-detector reading is *maximal*. This marks the point at which the axis of polarizer 2 coincides with the plane of polarization of light.

To estimate the precision of this method, we suggested that students repeat the measurement 10 times and determine the 95% confidence limits. Typical results from these 10 measurements are given in Table 1. One can see that the variation in measurements of the orientation of the polarization

Table 1. Orientation of Light-Polarization Plane Based on Maximum of Light-Detector Reading

Without Carvone	With Carvone
287°	332°
288°	334°
287°	332°
281°	335°
280°	330°
280°	336°
279°	331°
280°	336°
286°	336°
285°	329°

Table 2. Orientation of Light-Polarization Plane Based on Minimum of Light-Detector Reading

Without Carvone	With Carvone
16°	58°
11°	54°
10°	56°
14°	54°
10°	54°
11°	56°
14°	54°
10°	53°
14°	55°
10°	56°

plane both with and without the sample turns out to be about 2°. The results therefore yield 95% confidence limits for the angle of optical rotation α of about 4°. Considering that the mean value of α from this series of measurements is about 50°, only 6° from the above value of $\alpha_2 = 56.1°$, the precision of this approach is clearly not good enough for meaningful comparisons of α and α_2 using eqs 2 and 3. Thus, students can see that a better method of determining α is needed.

At this point, students are guided to think about the dependence of the magnitude of the signal from the light detector on the angle θ between the axis of polarizer 2 and the plane of polarization of light. The question "What characteristics of this dependence, do you think, determine the accuracy of the experiment?" is posed. The students soon realize that since the polarization plane (angle) is being estimated by monitoring the signal from the light detector, the method should be more accurate the steeper this dependence is. They further understand that only the component

$$E = E_0 \cos \theta \qquad (4)$$

of the electrical vector E_0 of the oncoming light is allowed through the polarizer (see Fig. 2a). Obviously, the dependence of $E = E(\theta)$ has the shape depicted in Figure 2b. By searching for the polarizer 2 orientation where the axis of polarizer 2 coincides with the plane of polarization of light (as described above) they have been using the point where $\theta = 0$ (the point indicated by arrow 1 in Fig. 2b). Clearly, the slope of the dependence of $E = E(\theta)$ at that point is zero, making it the

worst of the possible bases for their measurements! It typically seems to them that the best basis is given by the point where $\theta = 90°$ (the point indicated by arrow 2 in Fig. 2b), and in fact, the magnitude of the slope of the $E(\theta)$ dependence is maximal at this point. Therefore, the students conduct a new series of 10 experiments in which they measure the polarization plane by tuning to the *minimum*, rather than the maximum, of the signal (Table 2). After determining the 95% confidence limits they are astonished to see that they essentially did not decrease. Naturally, the next assignment is: "Determine why your theory didn't work, and modify your method in order to achieve better accuracy."

It takes students a while to determine the reasons for the discrepancy. Of course, their mistake was that the detector signal is proportional to the light intensity, I, rather than the magnitude of the electric vector E. In turn, as they know from their physics course, $I = aE^2$ (where a is a constant). Substituting the expression for E from eq 4, students find the true dependence of the signal on the angle θ:

$$I = aE_0^2 \cos^2 \theta \qquad (5)$$

which is depicted by the solid line in Figure 3. They can immediately see that the slope of the curve $E = E(\theta)$ is zero both for $\theta = 0°$ and $\theta = 90°$, and thus both of their previous attempts were equally bad!

What they need now, in order to determine the point in the graph where the true slope is maximal, is some calculus. Clearly, at the point where the first derivative is maximal, its derivative (that is, the second derivative of $I(\theta)$, I_θ'') must be equal to zero. I_θ'' can be found from eq 5:

$$I_\theta'' = -2aE_0^2(\cos^2 \theta - \sin^2 \theta) = -2aE_0^2 \cos(2\theta) \qquad (6)$$

Therefore the maximum lies where $\cos(2\theta) = 0$ (i.e, $2\theta = 90°$) and thus $\theta = 45°$ (the point indicated by arrow 3 in Fig. 3). Since $\cos 45° = \sqrt{2}/2$, the intensity at this point is equal to $(\sqrt{2}/2)^2 = 0.5$ of the maximal intensity I_{max}. Taking into consideration the intensity I_{min} of the background radiation, we find that the intensity at the point of interest, $I_{45°}$, is equal to

$$I_{45°} = (I_{max} - I_{min})/2 + I_{min} = (I_{max} + I_{min})/2 \qquad (7)$$

Thus, the subsequent strategy of the "most accurate" method is as follows. Students measure the maximal reading I_{max} of the light detector by aligning the axis of polarizer 2 parallel to the plane of the light polarization, and the minimal reading I_{min} (determined by the background radiation) by making it perpendicular to the plane of polarization.[2] They then calculate the value of $I_{45°} = (I_{max} + I_{min})/2$, rotate the
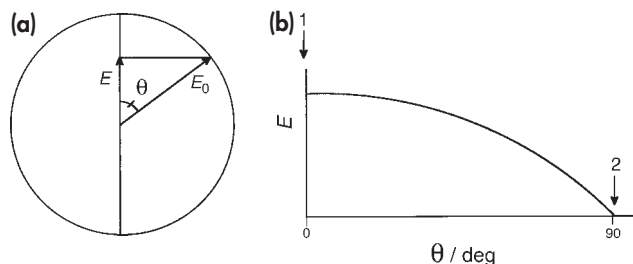

Figure 2. (a) Action of the polarizer on an E vector. (b) Dependency of the magnitude of the signal on the angle θ that the students initially expect from (a).
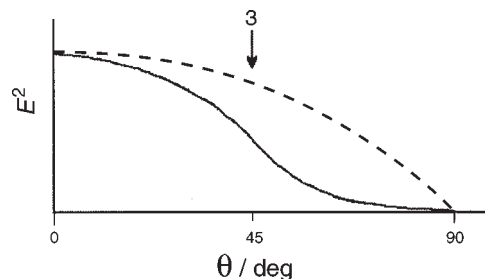

Figure 3. The true dependency (solid line) of the magnitude of the signal on the angle θ resulting from $I = aE^2$. Arrow 3 indicates the optimal point for accurate measurements

Table 3. Orientation of Light-Polarization Plane Based on Light-Detector Reading Halfway between Maximum and Minimum

Without Carvone	With Carvone
327°	16°
327°	16°
327°	16°
327°	16°
326°	16°
327°	16°
327°	16°
327°	16°
327°	15°
327°	16°

polarizer's holder until the intensity drops to the level of $I_{45°}$, and take the angle reading from the holder's scale. Repeating this procedure 10 times with and without the sample (Table 3), they can determine that the 95% confidence limits for the angle of optical rotation α is now reduced to about 1°. Thus, the students can effectively complete their assignment and find that their data are better described by the modified version of the Drude equation (eq 3).

Summary and Concluding Remarks

We have described a new lab for the determination of the optical activity and optical rotatory dispersion (ORD) of a compound. First our students determine the optical activity of a compound using the standard polarimeter (λ = 589 nm). Then they are given a He–Ne laser with a light detector and a polarizer and are asked to design the most accurate method for determining the angle of rotation for this second wavelength (λ = 633 nm). The method of guided inquiry is used throughout this part of the lab. The students ultimately should come up with the idea of using the orientation of the polarizer 2 where the intensity I of light exiting the polarizer is half of the sum of the minimal and maximal values; this is the point where the slope of the $I(\theta)$ curve is maximal and thus provides the most accurate data. They then analyze the results and find that they are better described by the modified version of the Drude equation (eq 3).

We wish to point out a distinct feature of the way the laser is used in this lab. Many other laser-based laboratories (see, for example, ref *8*) involve quite complex instrumentation, which might appear to be just a black box to an average student (*9*). In our lab (just as in papers *9* and *10*, published recently in this *Journal*), the laser serves simply as a light source. The other equipment involved is very simple and the general function of each device is transparent, which increases the students' level of self-confidence and understanding during their exploratory lab work.

The experiment described here is sensitive enough to observe optical rotary dispersion at wavelengths that can readily be reproduced in most undergraduate laboratories.

Paradoxically, that the difference between the optical rotations at these wavelengths is not very large is beneficial for the purposes of our lab, as this allows the students to better understand the need to design lab methods of higher accuracy. On the other hand, additional measurements nearer the absorption maximum of the chromophore, at shorter wavelengths in the case of most cyclohexanone derivatives, would be expected to illustrate larger changes in optical rotation near the absorption maximum and would provide a useful extension to this laboratory exercise. Also, determining the optical rotation of the sample at a third wavelength would extend the range of measurements and give the students a better idea of the wavelength dependence of the optical rotation.

This lab seems well suited to be conducted as an interdisciplinary laboratory. Indeed, the topics of optical activity and ORD are traditionally considered as pertaining mostly to the organic curriculum, whereas the methods used in the "laser" part of the lab clearly belong to physical chemistry. Finally, by placing emphasis on the design of the most accurate method of measurements, the lab helps to prepare the students for the scope of questions traditional for instrumental analysis.

Acknowledgment

Notes

1. One of the two polarizers (labeled "Polarizer-1" in Fig. 1) is needed only to make the radiation from the source plane-polarized. If the output of the laser is plane-polarized with a stable orientation then only one polarizer (labeled "Polarizer-2" in Fig. 1) is needed.

2. It is easy to get very accurate readings for both I_{max} and I_{min} owing to the zero slope of the dependency $I(\theta)$ at $\theta = 0°$ and $\theta = 90°$.

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