1 / VOL. 2, NO. 5
THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
10.1007/s00897970147a

Laboratories and Demonstrations

Using Lasers to Demonstrate the Concept of Polarizability:

Variations in the Refractive Indices of the *o*-Halobenzenes

GERALD R. VAN HECKE*, KERRY K. KARUKSTIS, AND J. MICHAEL UNDERHILL
Department of Chemistry
Harvey Mudd College
Claremont, CA 91711
gerald_vanhecke@hmc.edu

Using a simple 633-nm He/Ne or diode laser, the variation of the refractive indices of four ortho-substituted dihalogenated benzenes can be obtained, demonstrating the phenomenon of polarizability. In addition, this exercise is an excellent display of the correspondence between the properties of a chemical system on the macroscopic level and the characteristics of the molecule on a microscopic scale.

As a formal definition, the polarizability of a molecule is described as the ease with which an electric field can deform the electronic charge distribution of a molecule.

Introduction

The fundamental concept of *polarizability* is often a difficult notion for general chemistry students to visualize and comprehend. A confusion with the concept of polarity commonly exists. Students typically recognize that polyatomic molecules, consisting of covalent bonds, may or may not possess a permanent dipole moment depending on the polarity of the bonds and the symmetry of the molecule. All molecular covalent compounds, however, exhibit an instantaneous distortion of electron distribution that can induce a dipole moment in the neighboring molecule. As a formal definition, the polarizability of a molecule is described as the ease with which an electric field can deform the electronic charge distribution of a molecule. The series of diatomic halogens often serves as an example of the variation in polarizability with the number of electrons in (and hence the size of) the atoms in a molecule.

This demonstration uses *refractive index*, a macroscopic property of liquids, to reveal the variation in polarizability of a series of ortho-substituted dihalogenated benzenes. Liquids can be characterized by their refractive index, defined as the ratio of the speed of light in a vacuum to the speed of light through the liquid medium. Incident light may be viewed as inducing an oscillating dipole moment that radiates light at the frequency of the oscillation. The delay in phase of the induced radiation relative to the incident radiation results in a slower propagation of light in the nonvacuum; hence, the values of refractive indices are always greater than 1. The magnitude of the refractive index varies with the polarizability of the molecule; the more effective the distortion of molecular electronic distributions as a consequence of larger polarizabilities, the greater the refractive index. Refractive indices also depend on the frequency of incident light, increasing as the frequency (thus the energy) of the incident radiation increases. The variation of refractive index with frequency is referred to as *dispersion*, the underlying principle governing the separation of the range of frequencies of white light into the component frequencies upon refraction by a glass prism.

The disubstituted ortho-halogenated derivatives of benzene exhibit a wide range of molecular polarizabilities arising from the halogen substituents. The refractive indices at 20 °C measured using the sodium D line are: $C_6H_4F_2$, 1.44; $C_6H_4Cl_2$, 1.55; $C_6H_4Br_2$, 1.61; and $C_6H_4I_2$, 1.72. The refractive index increases as the halogen atomic number increases, consistent with both the larger size of the halogen atom and the larger number of electrons as one proceeds from fluorine to iodine. The demonstration described below uses the variation in the extent of refraction or bending of laser light as it passes through samples of the ortho-dihalogenated benzenes to illustrate the variable polarizabilities of the halogen substituents. For the substituent sequence $F \rightarrow Cl \rightarrow Br \rightarrow I$, the change in the refraction of the laser light is dramatic. To extend the demonstration, the use of lasers of different frequencies (e.g., red- and green-emitting helium-neon lasers) effectively illustrates the phenomenon of dispersion, with

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

higher-energy radiation (shorter wavelength) exhibiting a higher degree of refraction than longer wavelength light.

Experimental

Materials

1,2-difluorobenzene (CAS # 367-11-3), 1,2-dichlorobenzene (CAS # 95-50-1), 1,2-dibromobenzene (CAS # 583-53-9), and 1,2-diiodobenzene (CAS # 615-42-9) are available from Aldrich and can be used without further purification.

A helium/neon (633 nm, red, 1 mW) or diode laser, NMR tubes, and a wood mounting block are needed for the single-beam demonstration. The multiple-beam demonstration requires a beam splitter and several microscope slides. A green (543 nm) He/Ne laser, now commonly available, can also be used.

Safety Considerations

o-Dibromobenzene, *o*-dichlorobenzene, *o*-difluorobenzene, and *o*-diiodobenzene are irritants; avoid inhalation and contact. If spilled, assure adequate ventilation; absorb on sand and dispose of normally in a closed container. Additionally, these substances (especially *o*-difluorobenzene) should be kept away from open flames. This demonstration is effective in both small classrooms and large lecture halls; however, viewers should be protected from stray laser light reflected from glass surfaces by adequate shielding of the samples.

Procedure

Single Beam Demonstration

We have found that NMR tubes or other cylindrical pieces of glass with precision bores allow for excellent demonstration of differing refractive indices without the alignment difficulties associated with the use of prisms or similar geometric arrangements. In a cylindrical sample cell, the incident beam is internally reflected twice, allowing for the beam to exit close to 180° from incident (see Figure 1). The almost parallel incidence and exit can be used to arrange the optics of the demonstration in several ways. Figure 1 shows schematically the method used to obtain the results discussed below. Figure 2 is a photograph of the apparatus arrangement. Two other arrangements are illustrated in Figure 3. The demonstration depends on moving the sample tube(s) into the beam until a maximum-displacement

THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

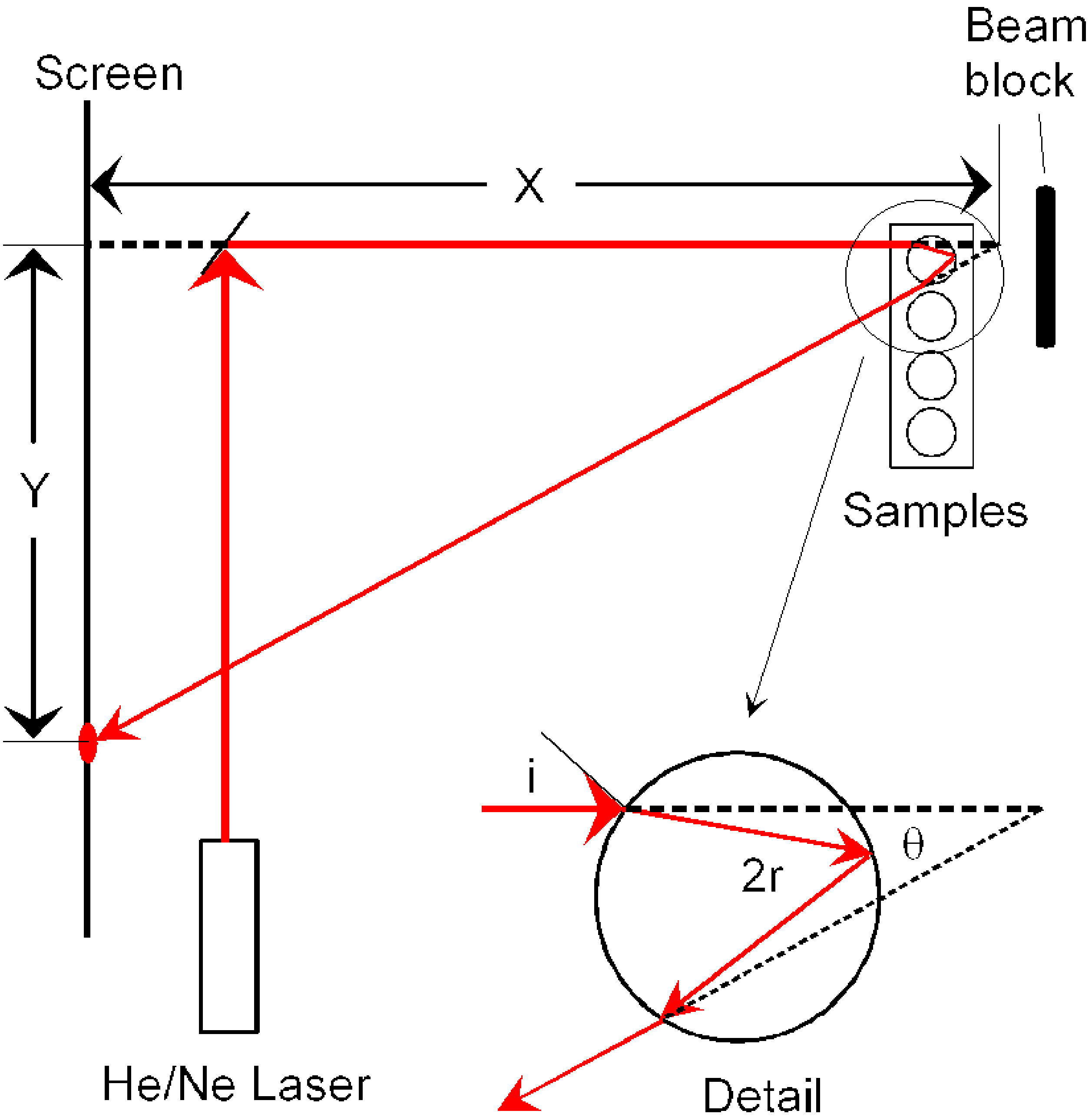

FIGURE 1. OPTICAL ARRANGEMENT OF A CYLINDRICAL SAMPLE CELL INDICATING THE TWO INTERNAL REFLECTIONS OF THE INCIDENT BEAM TO GENERATE AN EXIT BEAM CLOSE TO 180° FROM THE INCIDENT.

spot appears on the screen. The spot appears quite similar to a comet with a bright head and a tail of decreasing intensity. While several types of sample cells were tested, NMR tubes were decidedly the easiest to use, and very small samples achieved the same results as larger vials.

ISSN 1430-4171
THE CHEMICAL EDUCATOR
http://journals.springer-ny.com/chedr

S 1430-4171 (97)05147-X

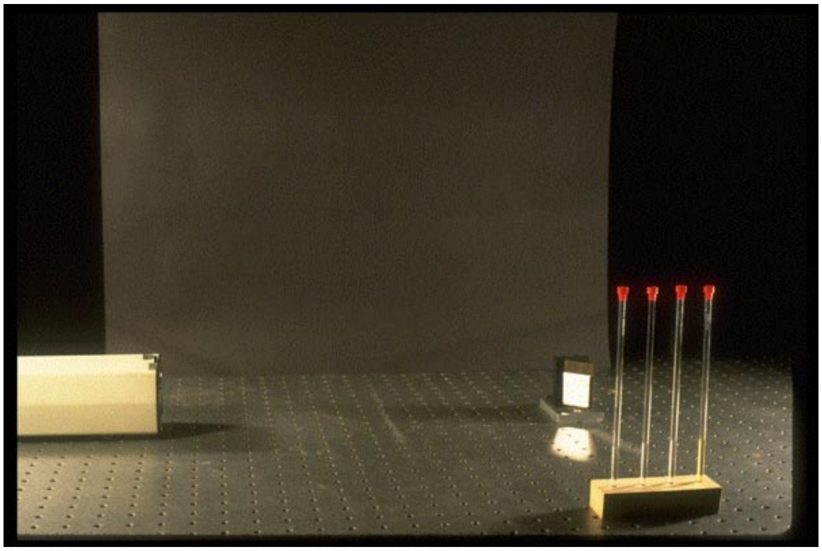

FIGURE 2. PHOTOGRAPH OF THE ARRANGEMENT OF THE APPARATUS FOR THE SINGLE-BEAM DEMONSTRATION.

To mount the tubes, a piece of wood approximately 1 × 4 in was drilled four times at equal spacing with an 0.196 in bit creating a snug fit of the tubes. The block was mounted to a plate with horizontal adjustment that allowed for scanning of the four samples. This entire assembly was set approximately 1 ft from the mirror as shown in Figure 1. Manually sliding the sample holder on top of the table was sufficient to accurately demonstrate the refractive indices of the *o*-halobenzenes. Similarly, it was shown that when aligned to yield a bright maximum, manually switching the tubes in a single hole of the block worked as well.

Some key points to assure reliable and safe results are:

1. Make sure the samples are far enough from the laser to allow for the maxima to be observed on your target surface.

2. Use a drill press if possible to drill the sample holder. Deviations from normal will shift the exit beam.

3. Adequately shield the samples. Stray light is emitted from the tubes at virtually all angles.

4. Seal the NMR tubes under vacuum to retain the samples and minimize exposure to the samples.

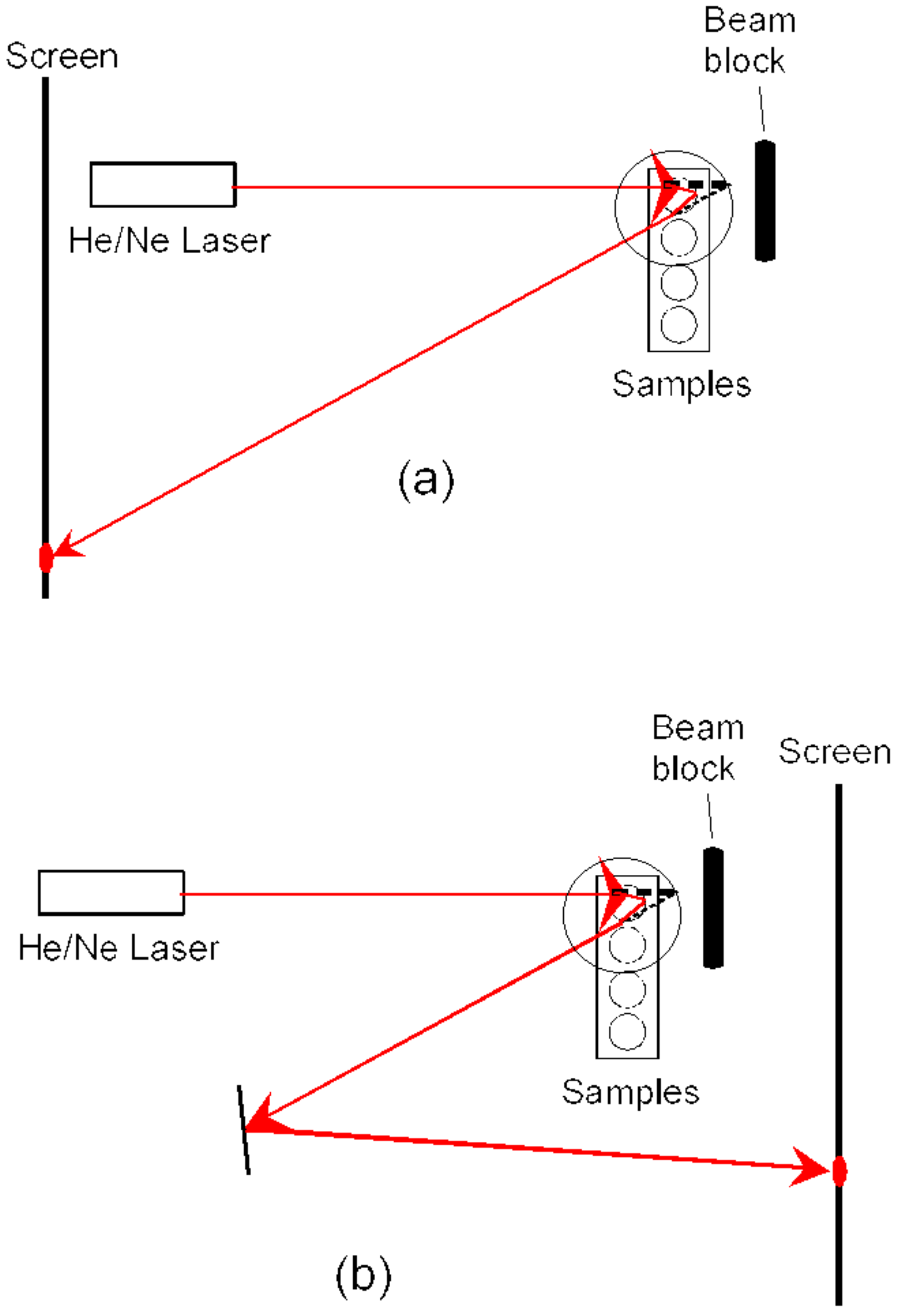

FIGURE 3. ALTERNATIVE APPARATUS ARRANGEMENTS.

Additionally, the *o*-halobenzenes tend to be light sensitive (especially *o*-diiodobenzene), so care in storage is recommended. When the above steps are followed, a simple and very effective means of demonstrating a rather interesting element of physical chemistry results.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

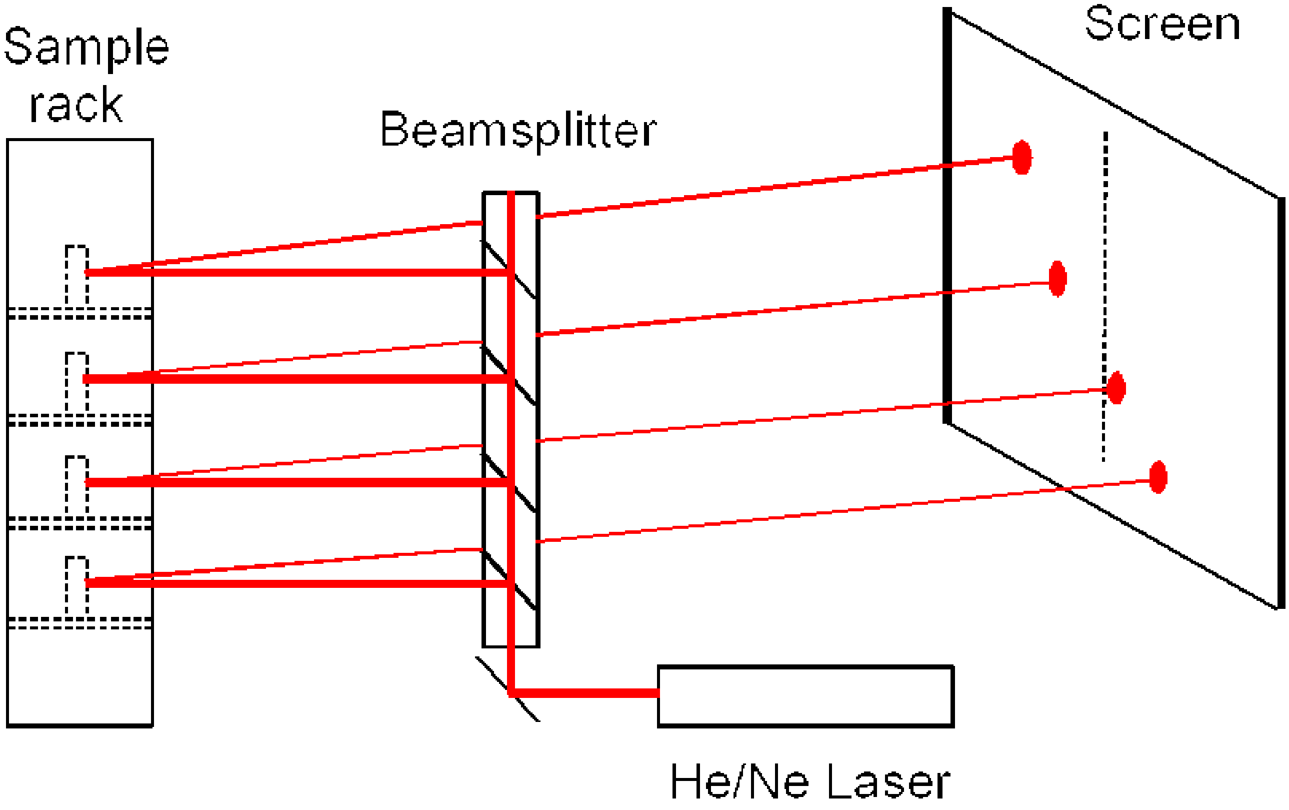

FIGURE 4. BEAM-SPLITTER APPARATUS FOR SIMULTANEOUS PROJECTION OF ALL SAMPLE REFRACTED BEAMS.

Multiple Beam Demonstration

For a more complex, yet more visually appealing, approach to the demonstration described previously, we employed a vertically mounted beam splitter to obtain four parallel horizontal beams in a vertical array. The beam splitter consisted of four microscope slides mounted at 45° angles inside a machined aluminum casing as diagrammed in Figure 4. The beam splitter was then mounted vertically and a mirror was mounted beneath it to route the laser beam from horizontal to vertical and up through the beam splitter (see Figure 4). The optical layout was that of Figure 3a. As the vertical beam struck each successive microscope slide, the beam was split to ultimately yield four parallel horizontal beams with equal vertical spacing. At this point, the demonstration can be thought of simply as four simultaneous repetitions of the previously described setup (Figure 3a) with a sample tube needed for each of the four beams. To hold the samples at the rather large distance of 2 ft from the beam splitter, necessary to avoid the exit beams colliding with the beam splitter itself, a wooden shelving system was built. The shelving system acted as both a sample holder

THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

and a shield for the stray light. The NMR tubes were cut to lengths of approximately 1.5 in and caps were placed at both ends. One of the two caps was glued to a small piece of sheet metal to act as a base that keeps the tubes upright on the sample shelves. With this apparatus a manual adjustment of the tubes on the sample rack to achieve bright maxima allows viewing of all four of the samples at once.

Results and Discussion

Figure 5 is a composite photographic image of the demonstration results and shows the change in position of the displaced spot as a function of substance and wavelength. The top two displacements are for the difluoro derivative, then, in succession: the dichloro, the dibromo, and the diiodo derivatives. The displacements for the green and red He/Ne lasers are obvious from the colors. For either wavelength of incident light, the beam displacement varies regularly as the polarizability of the liquid changes. With increasing polarizability (and therefore refractive index) of the sample, the displacement decreases.

What might seem strange is the trend of decreasing displacement with increasing refractive index. While the refractive indices noted earlier were obtained using sodium-D-line light (589 nm), the trends in the refractive indices of these compounds for green and red light should be the same. The seemingly opposite behavior of displacement (i.e., decreasing displacement with increasing refractive index) is correct, however, because of the optics of the sample cell and the refractive indices involved. For an approximately constant sample distance from the screen, the displacement Y (see Figure 1) is given by [1–3]:

$$\theta = 4r - 2i$$

$$Y = X\tan\theta = X\tan\left[4\sin^{-1}\left(\frac{4-n^2}{3n^2}\right)^{1/2}\right] - 2i$$

A plot of tan θ for various values of refractive index n with angle i of incidence set constant to 60° is given in Figure 6. For small n, around the value of water (1.33) the displacement increases with increasing n. For $n > 1.4$, the displacement (a function of i) actually decreases with increasing n, as observed in this demonstration.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

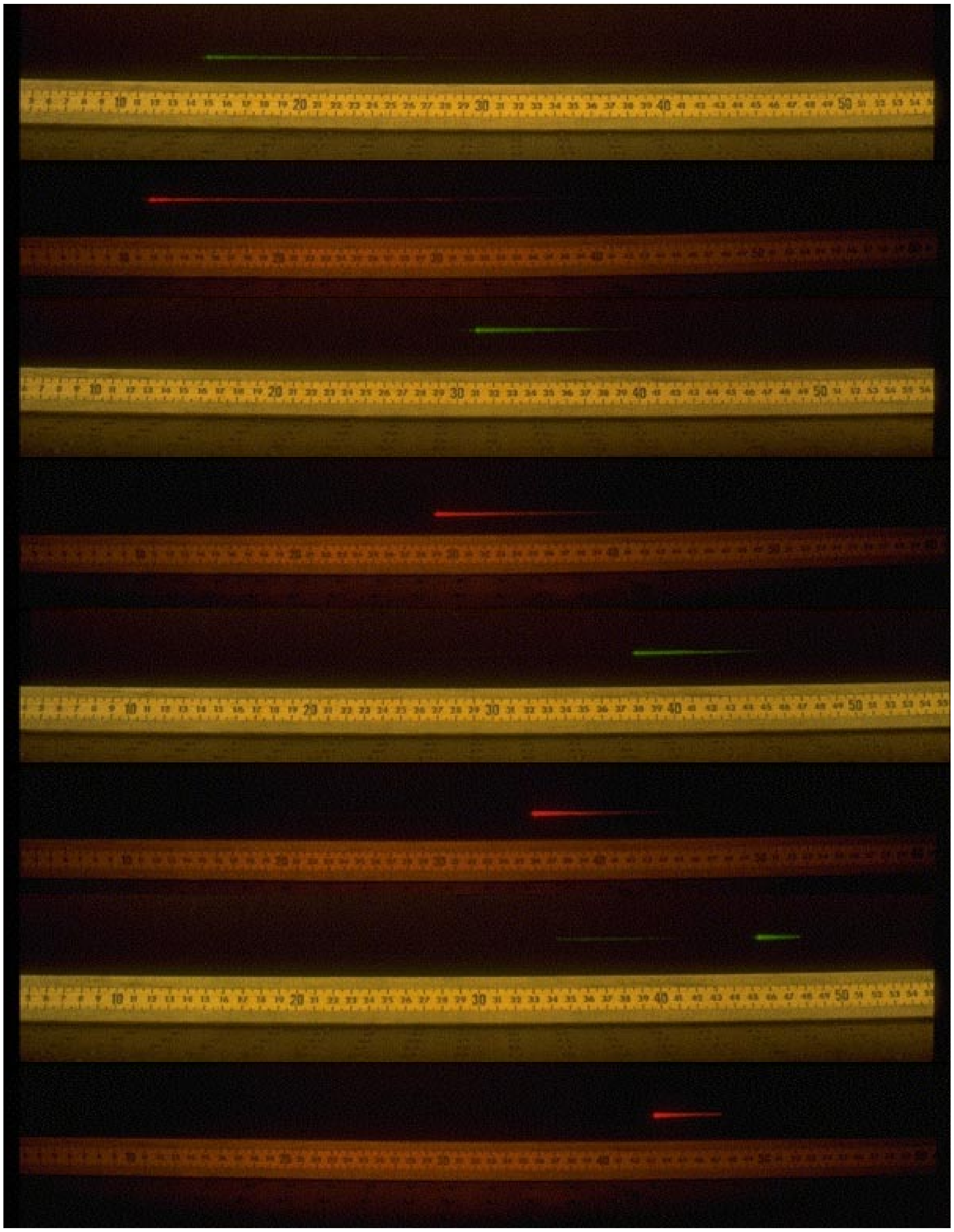

FIGURE 5. A COMPOSITE PHOTOGRAPHIC IMAGE OF THE DEMONSTRATION RESULTS SHOWING THE CHANGE IN POSITION OF THE DISPLACED SPOT AS A FUNCTION OF THE *O*-DIHALOGENATED BENZENE AND WAVELENGTH OF THE INCIDENT LASER BEAM. THE DISPLACEMENTS, READING FROM TOP TO BOTTOM IN PAIRS FOR THE GREEN AND RED INCIDENT LIGHT, ARE FOR THE DIFLUORO, THE DICHLORO, THE DIBROMO, AND THE DIIODO DERIVATIVES, RESPECTIVELY. FOR EITHER WAVELENGTH OF INCIDENT LIGHT, THE BEAM DISPLACEMENT DECREASES WITH INCREASING POLARIZABILITY (AND THEREFORE REFRACTIVE INDEX) OF THE LIQUID SAMPLE.

The observed dependence of n on wavelength is as expected for a substance that exhibits a normal dispersion such as shown in Figure 7 [4]. Thus, $n_{\text{green}} > n_{\text{red}}$ means

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

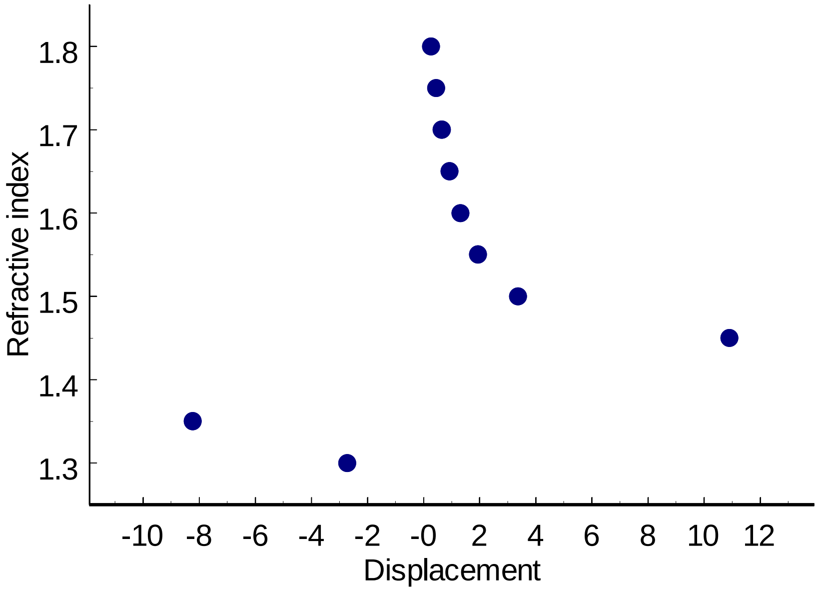

FIGURE 6. A PLOT OF TAN θ FOR VARIOUS VALUES OF REFRACTIVE INDEX *n* WITH ANGLE OF INCIDENCE *I* SET CONSTANT TO 60°. FOR SMALL *n*, THE DISPLACEMENT INCREASES WITH INCREASING *n*. FOR *n* > 1.4 (AS IS THE CASE FOR THE FOUR *O*-DIHALOGENATED BENZENES IN THIS DEMONSTRATION), THE DISPLACEMENT DECREASES WITH INCREASING *n*.

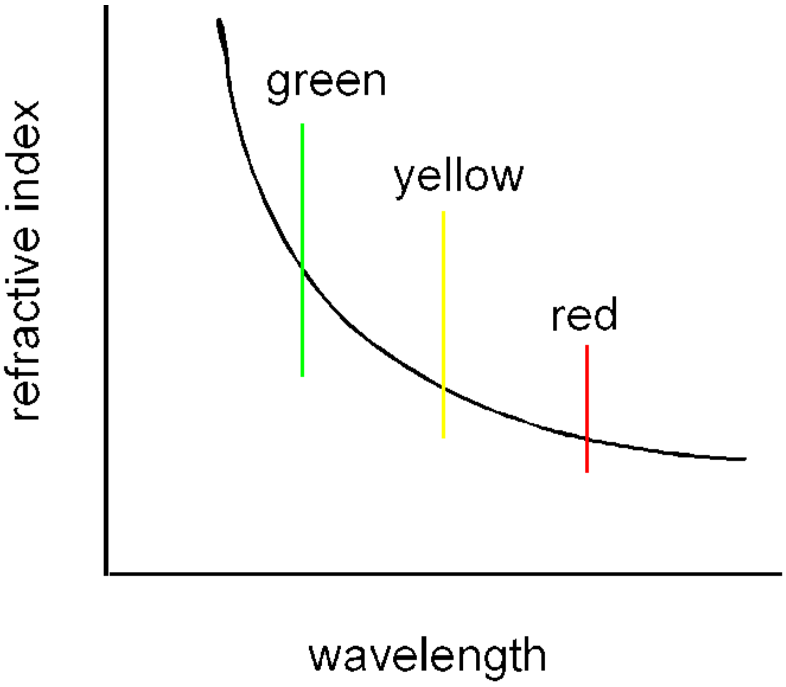

FIGURE 7. THE DEPENDENCE OF REFRACTIVE INDEX ON WAVELENGTH FOR A SUBSTANCE THAT EXHIBITS A NORMAL DISPERSION.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)05147-X

that, for our demonstration geometry, displacement(green) < displacement(red). If a dye laser were available and tunable to the sodium D line, the observed displacements should be between the red and green values observed here for each substance.

A plot of displacement versus molecular weight is one way to qualitatively connect polarizability with other molecular properties.

The series of compounds used here have permanent dipole moments. Using the 1,4-disubstituted derivatives would illustrate changes in polarizability without any influence due to changing dipole moments. Unfortunately, all of the 1,4-dihalobenzenes are solids at room temperature.

Conclusion

This laser demonstration provides an easy and striking visualization of the effect of molecular structure on refractive index and thus on polarizability.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support of the National Science Foundation through an ILI USE 8851387 grant for a multifunctional laser laboratory and through an USE 9155909 Curriculum Improvement grant directly for the development of laser demonstrations. We were also assisted by funds given to Harvey Mudd College by Kenneth Jonsson to support innovative uses of lasers. Several undergraduates participated in testing and developing this demonstration. We thank Rebecca Flitton, Micah Gearhart, Josiah Brown, and Steve Bordelon for their efforts on this project.

REFERENCES

1. Spencer, B. Zare, R. N. *J. Chem. Educ.* **1988**, *65*, 835.
2. Noll, E. D. *Phys. Teach.* **1973**, *11*, 307.
3. Noll, E. D. *Phys. Teach.* **1973**, *11*, 309.
4. Jenkins, F. A.; White, H. E. *Fundamentals of Optics*, 3rd ed.; McGraw-Hill: New York, 1957, p 466.