Refractive-index measurements with a Pellin-Broca prism apparatus

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An experimental system is described for measuring refractive indices of liquids and solids over a wide spectral range from the near IR to the near UV. A Pellin-Broca prism is used as the dispersing element. The obtained accuracy is $\Delta n = \pm 10^{-4}$.

I. Introduction

The absolute phase refractive index n relates the phase velocity v in matter to the vacuum light velocity c ($n = c/v$). It is determined by the molecular polarizability of the medium and gives insight to the interaction of light with matter and the structure of substances.[1-3] Additionally the group refractive index n_g is needed to describe light pulse propagation,[4,5] which is defined as the ratio of vacuum light velocity to group velocity v_g in matter[6] ($n_g = c/v_g$).

Various techniques have been developed to measure the refractive index n (for reviews see Refs. 2, 7, and 8). For liquids and solids most methods use the refraction or total reflection of light beams at prisms. The refractive indices of gases are generally measured with interferometers. The spectral range of commercially available refractive-index instruments is often limited to the sodium D line (wavelength $\lambda_D = 589.3$ nm) or some discrete lines of spectral lamps in the visible. The group refractive index n_g may be calculated from the wavelength dependence of the refractive index $n(\lambda)$. Direct measurements of the group refractive index are scarce.[9]

In this paper we describe a versatile apparatus for determining the phase refractive indices of liquids and solids. The wavelength may be continuously varied. Measuring phase refractive indices at closely spaced frequencies allows accurate calculation of the group refractive index. Various light sources such as tungsten halogen lamps, high-pressure xenon or mercury arc lamps, spectral lamps, or lasers may be used. A gen-

eralized Pellin-Broca prism is used as the dispersing element (hollow prism for liquids; prisms have to be formed from substances under investigation for solids). A spectrometer is used to select single frequencies for the measurements. The refracted light is detected with a silicon diode array detector. The 350–1100-nm spectral range is covered with a tungsten halogen lamp and visible optics. The spectral range may be extended down to 220 nm with xenon or mercury arc lamps and UV optics.

II. Method

The light passage through a generalized Pellin-Broca prism of arbitrary refracting angles α and β is depicted in Fig. 1. The light rays are refracted at the entrance and exit faces and totally reflected on the intermediate surface. The angles α and β are chosen nearly equal. Their magnitude is selected according to the range of refractive indices that should be covered (see below). In a restricted sense one speaks of Pellin-Broca prisms[4] when $\alpha = \beta = 30°$.

In the following we restrict our discussion to the propagation of linearly polarized light through liquids, isotropic solids, and uniaxial crystals with the c axis perpendicular to the electric field strength (ordinary rays). Within the cited limits the angular deviation δ of light is calculated by application of Snell's law of refraction at the entrance and exit faces and the law of reflection at the opposite side. The result is

$$\delta = 90° - \beta + \alpha - \varphi_I$$
$$+ \arcsin\left(n_r\left\{\sin\left[\alpha + \beta - \arcsin\left(\frac{1}{n_r}\sin\varphi_I\right)\right]\right\}\right), \qquad (1)$$

where $n_r = n/n_A$ is the relative refractive index, n is the absolute phase refractive index of the substance under investigation, and n_A is the absolute refractive index of the surrounding air. Equation (1) allows n_r to be calculated when angles α and β of the Pellin-Broca prism, the ray deviation angle δ, and the entrance angle φ_I are known. A computer program is used to determine n_r
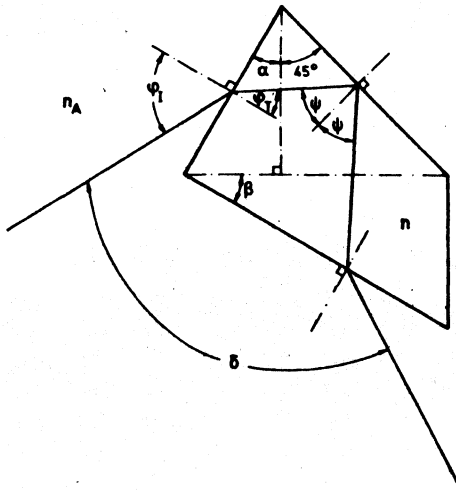
Fig. 1. Ray tracing through a general Pellin-Broca prism: n_A, absolute phase refractive index of air; n, absolute phase refractive index of liquid or solid.

from the measured incident angle φ_I (δ, α, and β are fixed).

If $\delta = 90°$ and $\alpha = \beta$, Eq. (1) reduces to

$$\varphi_I = \arcsin\left(n_r\left\{\sin\left[2\alpha - \arcsin\left(\frac{1}{n_r}\sin\varphi_I\right)\right]\right\}\right), \quad (2)$$

which has a solution for

$$\sin\varphi_I = n_r \sin\alpha. \quad (3)$$

Equation (3) is Snell's law for the symmetric path of light rays through the Pellin-Broca prism ($\alpha = \varphi_T$).

The dependence of the relative refractive index $n_r = n/n_A$ on the entrance angle φ_I is plotted in Fig. 2 for various prism angles $\alpha = \beta$ and an angular deviation $\delta = 90°$ [Eq. (2) or (3)]. Large α angles give high resolution (n_r varies slowly with φ_I), but the refractive-index range is limited (small upper limits of n_r). The selection of α depends on the expected range of refractive indices to be measured.

The accuracy of the refractive-index measurement may be estimated by calculating the variation of n_r with changes of φ_I. From Eq. (3) one finds

$$\Delta n_r = \frac{\cos\varphi_I}{\sin\alpha}\Delta\varphi_I; \quad (4)$$

Δn_r is small (high accuracy) for large entrance angles φ_I and large refracting angles α.

The absolute phase refractive index $n = n_r n_A$ and the group refractive index n_g at a fixed vacuum wavelength λ or frequency ν ($\nu = c/\lambda$) are connected by the relation[4]

$$n_g = \frac{n}{1 + \dfrac{\lambda}{n}\dfrac{\partial n}{\partial\lambda}} = \frac{n}{1 - \dfrac{\nu}{n}\dfrac{\partial n}{\partial\nu}}. \quad (5)$$

Measurement of n at two closely spaced wavelengths λ_1 and λ_2 allows one to calculate the group refractive index at $\lambda = (\lambda_1 + \lambda_2)/2$. {Here $\partial n/\partial\lambda$ is replaced by $[n(\lambda_1) - n(\lambda_2)]/(\lambda_1 - \lambda_2)$.}

The absolute refractive index of air depends somewhat on atmospheric pressure and temperature.[10] The
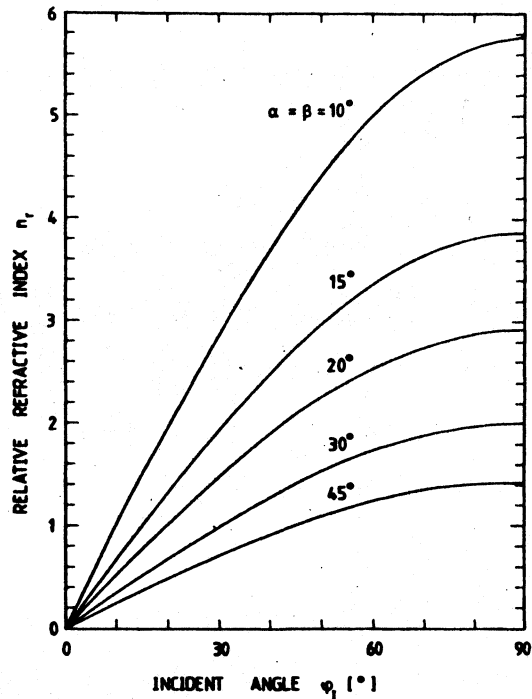

Fig. 2. Relative refractive index n_r vs incident angle φ_I of light to Pellin-Broca prism for various refracting angles $\alpha = \beta$. Deflection angle $\delta = 90°$.

following refractive-index dispersion equation of air (dry, with 0.03 vol. % CO_2) is rewritten from Ref. 10:

$$n_A(\bar{\nu},t,p) = 1 + \left(6.4328 \times 10^{-5} + \frac{2.94981 \times 10^6}{1.46 \times 10^{10} - \bar{\nu}^2} + \frac{2.554 \times 10^4}{4.1 \times 10^9 - \bar{\nu}^2}\right)$$
$$\times \frac{p_A(1.054915 + 8.3 \times 10^{-4}p_A - 1.2423 \times 10^{-5}p_A t_A)}{1.013877 + 3.7118 \times 10^{-3}t_A}, \quad (6)$$

where $\bar{\nu} = \nu/c$ is the frequency in cm^{-1}, t is the temperature in $°C$, and p is the pressure in bars ($n_A = 1.0002678$ at $\lambda_D = 589.3$ nm, $t_A = 25°C$, and $p_A = 1$ atm $= 1.01325$ bar).

III. Experimental

The experimental setup for the refractive-index measurement is depicted in Fig. 3: (a) the system for conventional light sources (tungsten halogen lamps, spectral lamps, xenon, or mercury arc lamps); (b) the experimental arrangement for laser sources (cw or pulsed).

The system with conventional light sources [Fig. 3(a)] uses an He–Ne laser to facilitate alignment. The alignment procedure is as follows. The He–Ne laser is focused to the slit $S1$ (0.1-mm width) with a cylindrical lens CL (focal length $f = 20$ cm), while lamp L is removed. The light is collimated with lens $L1$ ($f = 1.33$ m). the distance between S_1 and L_1 is equal to the focal length of $L1$. A right-angle prism P directs the light beam to the Pellin-Broca prism. To set a fixed deflection angle of $\delta = 90°$ the Pellin-Broca prism is replaced by a penta prism whose deviation from $\delta = 90°$ is <3 sec of arc. Lens $L2$ ($f = 1$ m) focuses the light
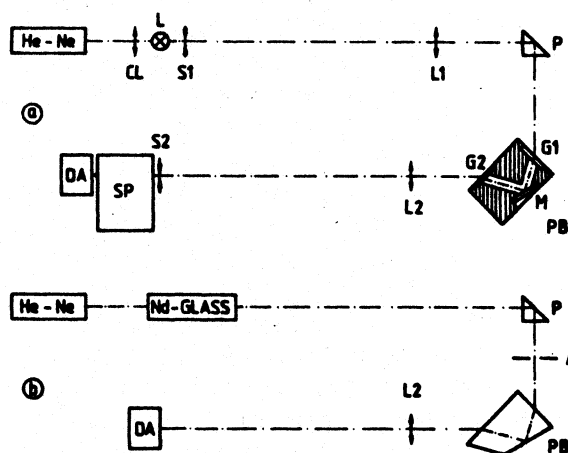
Fig. 3. Experimental setup for refractive-index measurement with (a) conventional light sources and (b) laser light sources. He–Ne, He–Ne laser; CL, cylindrical lens ($f = 20$ cm); L, light source; S1, slit (0.1-mm width); L1, achromatic lens ($f = 1.33$ m); P, 90° prism; PB, Pellin-Broca prism (1-cm hole diam); G1, G2, Suprasil windows; M, aluminum front mirror; L2, achromatic lens ($f = 1$ m); S2, slit (0.03-mm width); SP, spectrometer ($f = 25$ cm) with grating of 1200 lines/mm; DA, silicon diode array (Tracor DARSS). Nd:glass, mode-locked Nd:glass laser; A, aperture.

pulse to the entrance slit S2 (0.03-mm width) of the spectrometer. It is mounted on a translation stage to set the L2–S2 distance equal to the focal length of L2 (adjusted for each wavelength; at focal distance the detected signal is constant, independent of lateral passage through lens L2). The 25-cm spectrometer (1200-l/mm grating) is mounted on a translation stage for fine positioning perpendicular to the optical axis of L2. After adjusting the 90° deviation angle δ, the penta prism is removed, and the Pellin-Broca prism is inserted. The support consists of a precision 360° rotation table (resolution 0.001°, Micro-Control type RT 120) mounted on two crossed tilt platforms and a translation stage (movement perpendicular to optical axis of L2). The Pellin-Broca prism is rotated so that the He–Ne laser is reflected back to slit S1, and the zero position of the incident angle φ_I is obtained. Lamp L is now inserted. The Pellin-Broca prism is rotated until the wanted spectral component passes through slit S2 and is detected at the silicon diode array DA (Tracor DARSS-system) behind the spectrometer. To compensate concentric errors of the rotation table the angle φ_I is measured four times, whereby the start angle is changed by ~90° for each measurement. (Maximum deviation from average value was found to be 0.003°.) The refractive index vs wavelength may be recorded continuously when tungsten lamps, xenon, or mercury high-pressure arc lamps are used. Measuring the light wavelength behind slit S2 for two slightly different incident angles φ_I (difference 0.010°), the group refractive indices are easily determined [Eq. (4)].

Accurate measurement of refractive indices requires a precise determination of the angles α and β of the Pellin-Broca prism. For the investigation of liquids the

hollow Pellin-Broca prism form was drilled into a superrefined steel cylinder as indicated in Fig. 3(a). Plane-parallel plates G_1 and G_2 of fused silica are used as windows, and a plane-parallel aluminum mirror M is used as reflector. The parallelism of the plates and the mirror was measured with an autocollimation telescope. The small wedge of the plates (≤3 sec of arc) was positioned perpendicular to the plane spanned by the light path so that the plates are exactly parallel with the plane of refraction and reflection. The angles α and β are determined by measuring the angles between G1, M and G1, G2 with the rotation stage and the autocollimation telescope. Values of α = 30.142° ± 0.001° and β = 29.723° ± 0.001° were obtained for our sample. For the refractive-index measurement of solids a Pellin-Broca prism has to be cut out of the same material and polished. The angles α and β are measured in the same way as for the hollow prism. The accuracy of the 90° deflection angle δ was tested with a plane mirror mounted on the rotation stage instead of the Pellin-Broca prism. An angle of δ = (90 ± 5 × 10⁻⁴)° was measured.

The alignment of the system of Fig. 3(b) for the measurement of refractive indices at laser frequencies with cw or pulsed lasers is similar to the procedure described above. Again the position of δ = 90° beam deflection at the diode array is detected by insertion of a 90° pentaprism. The experimental arrangement is simpler since the entrance laser beam is already parallel. The refracted and reflected beam is directly focused on the diode array because the laser light is already monochromatic. A 1-mW He–Ne laser was attenuated and used as a cw light source. The system was also tested with a 5-psec pulse from a mode-locked Nd:glass laser.

The refractive index of liquids changes strongly with temperature.[2] For this reason the hollow Pellin-Broca prism is thermostated by temperature stabilized water circulation through a cylindrical enclosure.

Compared with the technique of minimum deviation through a triangular dispersion prism, the technique described here has the advantage of fixed 90° deviation. Only the Pellin-Broca prism has to be rotated, all other elements are fixed. The Pellin-Broca prisms are as easily fabricated as triangular dispersion prisms.

IV. Results

Continuous light sources allow spectral continuous measurement of refractive indices and calculation of group refractive indices. The absolute accuracy of the measured refractive index is determined by the accuracy of the measurement of the involved angles and the slit widths of S_1 and S_2. The angles α and β were measured to an accuracy of ±0.001°. The slit S_2 of the spectrometer accepts light within an angle of Δδ = 0.0017° (= slit width/focal length). The accuracy of the rotation table is ±0.001°, which gives an error of $\Delta\varphi_I$ = ±0.001°. Insertion of these error values into Eq. (1) gives an error of the refractive index of Δn = ±9 × 10⁻⁵ for φ_I = 45° and α = β = 30°. The error reduces for larger angles of φ_I, α, and β. Changes of refractive in-

dices (e.g., due to wavelength or temperature variation) are detected with an accuracy of $\Delta n = \pm 2 \times 10^{-5}$.

To test the apparatus refractive indices of the liquids (water and carbon tetrachloride) and the glass ($SF2$) were measured at various frequencies between 350 and 1100 nm. Obtained values at $\lambda = 589.3$ nm, air temperature $t_A = 22.5°C$, and pressure $p_A = 980$ mbar were (1) for H_2O $n_r = 1.3328$, $n = 1.3331$, $n_g = 1.3510$ ($t = 24.5 \pm 0.5°C$, no special treatment of distilled water, (2) for CCl_4 $n_r = 1.4608$, $n = 1.4611$, $n_g = 1.4886$ ($t = 20°C$), and (3) for Schott glass SF2 $n_r = 1.64754$, $n = 1.64797$, and $n_g = 1.7071$ (angle $\alpha = 30.0486°$, $\beta = 30.0069°$). The reported value is $n_r = 1.64752$ (Schott data sheet).

V. Conclusions

The apparatus described allows accurate and easy measurement of refractive indices over a wide frequency region from the UV to the IR. The spectral range may be further extended by suitable light sources and detectors. Any refractive-index value may be measured by proper selection of refraction angles α and β of the dispersing Pellin-Broca prism.

References

1. S. S. Batsanov, *Refractometry and Chemical Structure* (Consultants Bureau, New York, 1961).
2. N. Bauer and K. Fajans, in *Physical Methods of Organic Chemistry, Vol. 1*, A. Weissberger, Ed. (Interscience, New York, 1945), p. 653.
3. A. Penzkofer, H. Glas, and J. Schmailzl, Chem. Phys. **40**, 47 (1982).
4. E. Hecht and A. Zajac, *Optics* (Addison-Wesley, Reading, Mass., 1974).
5. R. Topp and G. C. Orner, Opt. Commun. **13**, 276 (1975).
6. L. Brillouin, *Wave Propagation and Group Velocity* (Academic, New York, 1960).
7. H. Kessler, in *Handbuch der Physik XVIII. Geometrische Optik, optische Konstante, optische Instrumente*, H. Geiger and K. Scheel, Eds. (Springer, Berlin, 1927), p. 623.
8. G. E. Fishter, in *Applied Optics and Optical Engineering, Vol. 5, Part 1*, R. Kingslake, Ed. (Academic, New York, 1967), p. 363.
9. D. B. McDonald and S. A. Rice, Opt. Commun. **32**, 416 (1980).
10. D. H. Rank, in *Advances in Spectroscopy, Vol. 1*, H. W. Thompson, Ed. (Interscience, New York, 1959), p. 76.

H. J. Bolle (Universitat Innsbruck) on the left and Thomas von der Haar (Colorado State University) photographed by P. Kopke (Meteorologishes Institut der Universitat Munchen) during the 1981 JAMAP meeting in Hamburg.