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2004 Metrologia 41 189

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# Using helium as a standard of refractive index: correcting errors in a gas refractometer

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Received 8 January 2004

Published 19 April 2004

Online at [stacks.iop.org/Met/41/189](http://stacks.iop.org/Met/41/189)

DOI: 10.1088/0026-1394/41/3/012

## Abstract

The refractive index of helium at atmospheric pressure can be determined from *ab initio* calculations in combination with careful pressure and temperature measurements. Therefore, helium can serve as a theory-based standard of refractive index; it might be used as a medium of known refractive index for high-accuracy interferometric length measurements or it can be used to characterize and correct errors in a gas refractometer. We have used helium to correct for pressure-induced distortions of two refractometers built by us, where both refractometers basically consist of a laser locked to the transmission maximum of a simple Fabry–Perot cavity. As a proof-of-principle of the helium-correction technique, we have used our device to measure the molar refractivity of nitrogen and we find reasonable agreement with previous measurements. When our two refractometers simultaneously measure the refractive index of a common nitrogen sample, we find that the two systems agree with each other within a few parts in  $10^9$ .

## 1. Introduction

Uncertainty in the refractive index of air often limits the attainable accuracy of interferometer-based length measurements. One possible strategy for improving such measurements is to use helium in place of air as the working medium for interferometry. Helium gas at atmospheric pressure is attractive because (1) its refractivity is one-eighth that of air and (2) the refractive index at a known temperature and pressure can be calculated from first principles with high accuracy. From a strictly theoretical standpoint, the uncertainty in the calculated refractive index of helium at atmospheric pressure is probably of the order of  $10^{-10}$ , where this uncertainty arises primarily from incomplete evaluation of quantum electrodynamic effects. (Note: there is no need to distinguish between *relative* and *absolute* uncertainty of the refractive index since  $n \approx 1$  in this application.) As a practical matter, the attainable uncertainty is usually set by the accuracy of helium pressure and temperature measurement or by residual impurities in the helium gas. Although uncertainties in the measurement of helium pressure and

temperature limit the attainable accuracy, the low refractivity of helium reduces these limitations by a factor of 8 relative to the corresponding uncertainties when determining air refractive index from environmental measurements.

Even when it is not practical to use helium directly as the medium for interferometry, we can use helium as a known standard of refractive index in order to characterize and correct errors in a gas refractometer. We have developed a simple gas refractometer based on a laser locked to the transmission maximum of a Fabry–Perot interferometer (hereafter designated FPI), and we use helium to correct for pressure-induced distortions of the FPI cavity. Changes in laser frequency track changes in refractive index as the interior of the FPI cavity is filled with gas or pumped out to vacuum. For an ideal cavity, the change in laser frequency is proportional to the change in refractivity going from the evacuated to the filled state. (Refractivity is  $n - 1$ , where  $n$  is the refractive index.) Since the evacuated state has a known refractive index  $n = 1$ , measuring the *change* in refractive index also tells us the *absolute* refractive index of the gas. A practical problem in implementing this scheme is the difficulty in accounting for distortions of cavity dimensions caused by the changing pressure. It is expected that our

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cavity length will be compressed by about 6 parts in  $10^7$  by atmospheric pressure [1]. As a consequence, if the material's bulk modulus is uncertain by 7%, then the refractive index can only be determined to an uncertainty of 4 parts in  $10^8$ . Furthermore, we have observed pressure-dependent changes in cavity dimensions that cannot be attributed to simple uniform compression [1]. Although we believe that these changes are probably associated with dissimilar materials in the cavity, we do not understand the changes in sufficient detail to model the distortion mathematically.

One method to overcome this problem is to employ helium gas at atmospheric pressure as a known reference because the refractive index of helium can be calculated accurately from first principles. Two similar procedures might be employed:

- (1) It is possible to map the cavity distortion as a function of pressure. Since the refractive index of helium is known, any discrepancy between the measured and known helium refractive indices can be interpreted as a cavity distortion.
- (2) Rather than tracking variations in refractive index as the cavity is evacuated, it would be possible to track the variation when the gas to be measured is replaced by helium at nearly the same pressure. That is, instead of using vacuum with  $n = 1$  as a known reference state, we would use helium at atmospheric pressure and its calculated index of refraction as the known state; thus pressure distortions are avoided.

Conceptually the two methods are identical: the helium serves as a theory-based reference standard against which the unknown gas can be compared. If the FPI cavities were perfectly stable over time, so that it was never necessary to return to the reference state, then there would be no significant practical differences in the two methods. However, it is necessary to periodically re-check the reference because of ageing of the spacer material or other effects that give rise to changes in the effective length of the FPI (of the order of 1 part in  $10^7$  per year).

Method (2) could be carried out, at least in principle, without the need for a vacuum pump, if sufficient helium were flushed through the apparatus to ensure purity. However, it is necessary to have good pressure and temperature sensors available to determine the helium refractive index. With method (1), the good sensors need only be present once—when the cavity distortions are calibrated initially—but in order to monitor slow temporal changes in cavity length it is necessary to pump out the cavity periodically to vacuum. The residual pressure of atmospheric gases must be less than 1 Pa, or at least measured with an uncertainty less than 1 Pa, in order to achieve  $3 \times 10^{-9}$  uncertainty in subsequent refractive index measurements.

Using either of these schemes, at some point in time it is necessary to determine helium pressure and temperature accurately, but the low refractive index of helium puts minimal demands on the required accuracy of the sensors.

## 2. Theoretical calculation of helium refractive index

The key to our method is knowing an accurate value for the refractive index of helium. At a known temperature and pressure, the refractive index can be determined to very high accuracy from *ab initio* calculations. There are several parts

to this calculation.

- (1) The refractive index can be determined from the Lorentz–Lorenz equation. This can be written in the form

$$\frac{n^2 - 1}{n^2 + 2} = A_R \rho + B_R \rho^2 + \dots \quad (1)$$

(see, e.g., Pendrill [2]). Here,  $n$  is the refractive index and  $\rho$  is the density in moles per unit volume.  $A_R$  is the molar polarizability, and the refractivity virial coefficient  $B_R$  accounts for the effect of two-body interactions on the refractive index.

- (2)  $A_R$  is proportional to the atomic or molecular polarizability  $\alpha$ :

$$A_R = \frac{4\pi}{3} N_A \alpha \quad (2)$$

where  $N_A$  is Avogadro's constant (see, e.g., Born and Wolf [3]).

- (3) For a non-ideal gas the molar density  $\rho$  is not related to pressure linearly but is given by

$$\rho = \frac{P}{Z N_A k T} \quad (3)$$

where  $P$  is the pressure,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature, and the compressibility factor  $Z$  for a non-ideal gas can be written as an expansion similar to (1):

$$Z = 1 + B(T)\rho + C(T)\rho^2 + \dots \quad (4)$$

$B(T)$  and  $C(T)$  are virial coefficients for the compressibility expansion.

The equations above implicitly allow the calculation of the refractive index in terms of  $A_R$  (or equivalently  $\alpha$ ),  $B_R$ ,  $B(T)$ ,  $C(T)$ , and helium pressure and temperature. Ignoring small terms non-linear in density, equations (1)–(3) imply that the refractivity (i.e.  $n - 1$ ) is proportional to  $\alpha/k$ , and thus the polarizability  $\alpha$  and the Boltzmann constant  $k$  are the parameters of greatest importance when calculating the refractivity at a known temperature and pressure. (This reasoning led Pendrill [2] to suggest that refractivity measurements could be used to improve knowledge of the Boltzmann constant.) The 2002 CODATA [4] recommended value for the relative standard uncertainty of the Boltzmann constant is  $1.8 \times 10^{-6}$ , and the relative uncertainty in  $\alpha$  is probably of somewhat smaller magnitude (as discussed later). These uncertainties will dominate the uncertainty of the calculated refractive index. The individual parameters that go into the calculated refractive index are discussed in detail below.

### 2.1. The atomic polarizability $\alpha$ and molar polarizability $A_R$

The atomic polarizability has been calculated, including relativistic effects to second order in the fine-structure constant, by Bhatia and Drachman [5]. This calculated value is probably limited in accuracy primarily because it does not include the effect of quantum electrodynamics. The Bhatia–Drachman

formula might be improved somewhat by replacing the static component of their polarizability with a term that includes QED, as has been calculated by Pachucki and Sapirstein [6], by Cencek *et al* [7], and most recently by Lach *et al* [8]. In reduced Rydberg units, the polarizability as a function of the frequency  $\omega$  is then given by

$$\alpha = 1.383\,191\,6 + 0.385\,530\,216\omega^2 + 0.127\,538\,95\omega^4 + 0.045\,731\,14\omega^6 \quad (5)$$

where the first term is based on Lach *et al* and the remaining terms are from Bhatia and Drachman.

There is good reason to believe that the *static* polarizability of helium (which determines the dielectric constant) can be calculated with an uncertainty well below 1 part in  $10^6$ . Over the past five years, independent calculations of the static polarizability have been in good agreement, and recently the value has been improved somewhat by inclusion of QED (which shifts the result by about 0.002%). The most recent calculation of Lach *et al* [8] has a relative uncertainty of  $2 \times 10^{-7}$ . The result of Lach *et al* differs from the value given in [6, 7] (which do not fully evaluate the QED correction and consequently have larger uncertainty) by only 5 parts in  $10^7$ .

In addition to the uncertainty in the static polarizability, it is necessary to consider the uncertainty in the frequency dependence of the polarizability. Both the static and frequency-dependent polarizability were calculated in [5], but the calculation did not include QED. However, it would seem somewhat unlikely that the neglect of QED in the frequency dependence would contribute greatly to the overall error in polarizability at visible wavelengths longer than 633 nm because the frequency-dependent terms are small; they contribute only 0.6% to the total polarizability at 633 nm. If QED produces the same fractional change in the frequency-dependent terms as the fractional change due to QED in the static term (2 parts in  $10^5$ ), then the resulting error in polarizability would be only 1 part in  $10^7$ . This naive order-of-magnitude argument works modestly well for other perturbations where results are known; in absolute terms, corrections arising from mass polarization and relativity are about 300 times larger in the static polarizability than in the dynamic terms, as can be seen by comparing Bhatia and Drachman's results of [5] with their earlier results for a non-relativistic, infinite mass system [9].

By coincidence, the QED correction to the *static* term largely cancels the effect of the other perturbations, giving nearly the same final result as the simple calculation for a non-relativistic infinite mass system. If the same cancellation were to occur in the dynamic terms, it would affect our final result at the  $10^{-7}$  level.

Recognizing that our  $1/10^7$  estimate of QED effects in the dynamic terms is only an order-of-magnitude guess, we somewhat arbitrarily assign an uncertainty to account for the neglect of QED in the dynamic terms that is ten times larger than this value (i.e.  $1 \times 10^{-6}$  relative uncertainty). The uncertainty of the static term is negligible in comparison, and thus the overall estimate for the uncertainty is  $\Delta\alpha/\alpha = 1 \times 10^{-6}$ . It is difficult to justify a lower uncertainty without a better understanding of the QED corrections in the dynamic terms. A lower uncertainty is not really needed for our current purposes; it may be noted that the  $1 \times 10^{-6}$  estimated relative

uncertainty in  $\alpha$  will give rise to an uncertainty of only  $3 \times 10^{-11}$  in the calculated value for the refractive index of helium at atmospheric pressure.

It is necessary to determine the molar refractivity (equation (2)) from the polarizability  $\alpha$  as given in reduced atomic units by equation (5). For  $^4\text{He}$ ,  $A_R$  in units of  $\text{cm}^3 \text{mol}^{-1}$  is related to  $\alpha$  by

$$A_R = \alpha \times \frac{4\pi}{3} N_A a_0^3 \left(1 + \frac{m_e}{m_\alpha}\right)^3 = 0.373\,956\,92\alpha \quad (6)$$

where  $N_A$  is the Avogadro constant,  $a_0$  is the Bohr radius, and  $m_e/m_\alpha$  is the electron to alpha-particle mass ratio. We have used 2002 CODATA values for the parameters. The most important uncertainty in the values of the physical parameters of (6) is a  $1.7 \times 10^{-7}$  relative standard uncertainty of the Avogadro constant.

As in [5], we replace  $\omega$  in reduced Rydberg units by  $\lambda$  expressed in nanometres using the relationship

$$\omega = \frac{4\pi a_0}{\alpha_f [1 - m_e/(m_\alpha + m_e)] \lambda} = \frac{91.139\,197\,92}{\lambda} \quad (7)$$

where  $\alpha_f$  is the fine-structure constant.

With this substitution and the conversion factor of (6), the molar polarizability becomes

$$A_R = 0.517\,254\,07 + \frac{1197.5410}{\lambda^2} + \frac{3.290\,677 \times 10^6}{\lambda^4} + \frac{9.800\,874 \times 10^9}{\lambda^6} \quad (8)$$

where  $A_R$  is expressed in units of  $\text{cm}^3 \text{mol}^{-1}$ , with an estimated relative uncertainty of  $1 \times 10^{-6}$  at optical frequencies.

At  $\lambda = 633 \text{ nm}$ , equation (8) yields  $A_R = 0.520\,263\,4(5) \text{ cm}^3 \text{mol}^{-1}$ . This value is seriously inconsistent with the two most recent experimental measurements. Achtermann *et al* [10] have determined  $A_R = 0.5213(1) \text{ cm}^3 \text{mol}^{-1}$ , and Birch [11] obtained a value of  $0.5220(3) \text{ cm}^3 \text{mol}^{-1}$ . In terms of the refractive index at atmospheric pressure, Achtermann's result is high by  $7 \times 10^{-8}$  and the result of Birch is high by  $1.1 \times 10^{-7}$ . If we are to believe the theoretical result, then we must assume that some surprisingly large errors (perhaps contamination of the helium) corrupted the experimental measurements.

Although the experimental results tend to erode our confidence in the theoretical value, there is indirect experimental evidence that supports the theoretical result and is inconsistent with the two direct measurements quoted above: (a) the static part of the polarizability as calculated by (8) is consistent with experimental measurements of the dielectric constant [12] within the scatter of experimental results (a standard deviation of  $2 \times 10^{-7}$  for measurements up to 7 MPa pressure) and (b) the frequency dependence predicted by (8) is consistent with experimental dispersion measurements of Mansfield and Peck [13] and with the more recent results of Velsko and Eimerl [14]. The agreement is particularly good with the results of Velsko and Eimerl, where their measured variation  $\Delta n$  in refractive index between 1064 nm and 532 nm differs by only  $1.2 \times 10^{-9}$  from the calculated value. Based on this indirect experimental evidence, it seems unlikely that the error in refractive index as calculated from the polarizability of equation (8) could exceed  $4 \times 10^{-9}$  at 633 nm. This is more than

an order of magnitude smaller than the observed discrepancy with Achtermann's results. Thus the indirect evidence largely negates the concerns raised by the direct measurements of molar polarizability.

### 2.2. The virial coefficients

In addition to the molar polarizability, the refractive index at a given temperature and pressure also depends somewhat on the virial coefficients  $B(T)$ ,  $C(T)$ , and  $B_R$ .

The coefficient  $B(T)$  has been calculated by Hurly and Moldover [15]. Their results, near room temperature, can be approximated as

$$B(T) = 13.028 - 0.0041T \quad (9)$$

where  $B(T)$  is expressed in  $\text{cm}^3 \text{mol}^{-1}$ , and the linear fit deviates from the numbers given by Hurly and Moldover by no more than  $0.001 \text{ cm}^3 \text{mol}^{-1}$  over the range 275 K to 325 K. This deviation is much smaller than the  $0.03 \text{ cm}^3 \text{mol}^{-1}$  estimated uncertainty of the theoretical calculation. The uncertainty in  $B$  gives rise to an uncertainty of  $4 \times 10^{-11}$  in the refractive index.

The compressibility virial  $C(T)$  is of negligible importance; the value near room temperature as given by Dymond and Smith [16] ( $\approx 100 \text{ cm}^6 \text{mol}^{-2}$ ) contributes to the calculated refractive index at atmospheric pressure by only  $6 \times 10^{-12}$ .

For the refractivity virial coefficient at 633 nm, we use

$$B_R = -0.032 - 0.0001T \quad (10)$$

where  $B_R$  is expressed in units of  $\text{cm}^6 \text{mol}^{-2}$  and the temperature  $T$  is between 273 K and 323 K. We estimate the uncertainty as  $0.007 \text{ cm}^6 \text{mol}^{-2}$ , which corresponds to a  $2 \times 10^{-11}$  uncertainty in the refractive index. The estimates for  $B_R$  and its uncertainty are based on calculations of Koch *et al* [17] plus the experimental and theoretical results cited in this reference.  $B_R$  has only a small effect on the refractive index (modifying the result by less than  $2 \times 10^{-10}$ ), and higher refractive virial coefficients are expected to have a negligible effect at atmospheric pressure.

### 2.3. Summary of the calculation

To summarize, we can calculate the refractive index for helium at a given temperature and pressure using the following procedure, easily implemented as a spreadsheet calculation:

- (1) Find  $B(T)$  from equation (9) or from [15].
- (2) Find  $Z$  from (4) using  $C(T) = 0$  and with  $\rho$ , expressed in  $\text{mol cm}^{-3}$ , given in first approximation as  $\rho = P/(N_A kT)$ .
- (3) Compute a refined value for  $\rho$  from (3).
- (4) Compute the molar polarizability,  $A_R$ , from (8).
- (5) Find  $(n^2 - 1)/(n^2 + 2)$  from (1), with  $B_R$  given by (10) at wavelengths near 633 nm.
- (6) Find the refractive index. If we define

$$z \equiv \frac{n^2 - 1}{n^2 + 2} \quad (11)$$

then it follows [5] that

$$n \approx 1 + \frac{3z}{2} + \frac{3z^2}{8}. \quad (12)$$

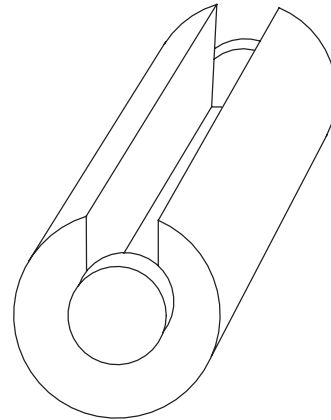


Figure 1. Schematic picture of the FPI cavity.

According to this calculation, the refractive index of helium for 633 nm radiation, at 101 325 Pa pressure and 20 °C, is 1.000 032 426 00(8), where the standard uncertainty ( $8 \times 10^{-11}$ ) arises from a root-sum-squares combination of (a) uncertainty from the theoretical calculation of  $\alpha$ , contributing  $3 \times 10^{-11}$ , (b) uncertainty in  $k$ , contributing  $6 \times 10^{-11}$ , (c) uncertainty in  $B(T)$ , contributing  $4 \times 10^{-11}$ , and (d) uncertainty in  $B_R$ , contributing  $2 \times 10^{-11}$ .

### 3. A refractometer based on a Fabry-Perot cavity

We can track changes in the refractive index of a gas using a laser servolocked to the transmission maximum of a dimensionally stable FPI cavity. As the refractive index of the air inside the cavity changes, the servo system changes the frequency of the laser so as to maintain a constant air wavelength in resonance with the cavity. Changes in laser frequency, measured as changes in the heterodyne beat between the servolocked laser and a fixed-frequency laser, can be used to measure the change in refractive index. This basic scheme has been used by several authors to measure refractive index [18–24].

We have constructed two Fabry-Perot cavities using mirrors on fused-silica substrates that are optically contacted to the ends of Zerodur<sup>2</sup> spacers. The Zerodur spacers were manufactured from a solid rod by sawing a rectangular channel that extends along the entire length of the rod and goes more than halfway through the centre (see figure 1). The channel forms the interior space of the Fabry-Perot resonator in a manner that is very open to the surrounding gas. Details of the cavity construction are described in a previous publication [1]. One cavity is approximately 452 mm long, while the second is much shorter (94 mm), so that we can study possible length-dependent errors. The chosen length ratio provides an efficient vernier to facilitate unambiguous identification of mode order, as discussed in [1].

For each FPI, a laser is locked to the cavity using a simple dither of the laser frequency, phase sensitive detection

<sup>2</sup> Commercial equipment and materials are identified in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

of the transmission maximum with a lock-in amplifier, and an integrating feedback loop to control the laser frequency. A helium–neon laser with piezoelectric control of the cavity length is locked to the long cavity, and a tunable diode laser operating at 633 nm is locked to the short cavity.

The two cavities are mounted next to each other in a chamber in which the temperature and pressure can be controlled. Thus, we can compare results from these two independent systems measuring essentially the same environment, although there are small temperature gradients between the two cavities. These gradients are measured by three pairs of thermocouple junctions wired in series, where each pair has one member in each cavity. From a strictly electrical standpoint, this arrangement should measure gradients with sub-millikelvin uncertainty, but large gradients are probably not measured so well (as discussed in section 6). The cavities are both mounted with one end suspended by a wire sling so that changes in the chamber dimensions do not produce stresses on the cavities.

The basic operation of the cavities is governed by the requirement that the air wavelength of the laser must be resonant with the cavity. If the mirrors are separated by distance  $l$  containing a medium with refractive index  $n$ , the frequency  $f$  of the laser must be

$$f = \frac{mc}{2nl} \quad (13)$$

where  $m$  is an integer and  $c$  is the speed of light in vacuum. For our purposes here, in the equation above we have ignored the Guoy phase shift (associated with the non-plane-wave cavity mode) and phase shifts associated with reflection from the mirrors. The Guoy phase shifts only affect our refractive index measurements at the  $10^{-11}$  level, too small to be of significance here. The primary influence of mirror reflective phase shifts occurs through an effect on the determination of the free spectral range; we will return to this point later. There is also a small change in the reflective phase due to changing refractive index within the cavity, but this is expected to cause  $<10^{-10}$  uncertainty in our results if the centre of the mirror reflective band lies within a few per cent of 633 nm.

For an ideal FPI, (13) implies that the gas refractivity  $(n - 1)$  is related to the initial cavity frequency under vacuum ( $f_i$ ) and to the final frequency under pressure ( $f_f$ ) according to

$$n - 1 = \frac{f_i - f_f + \Delta m(\text{fsr})}{f_f} \quad (14)$$

where  $\Delta m$  is the change in order and fsr is the free spectral range under vacuum ( $\text{fsr} = c/2l$ ). We currently determine  $\Delta m$  by comparing results from our two cavities, as described in [1]. It would also be possible to determine  $\Delta m$  by employing low-accuracy pressure and temperature sensors to give a first estimate of the refractive index and then use the FPI results to refine this first guess. For a 100 mm long cavity, a change of one order corresponds to a change in air pressure of 1200 Pa or a change in air temperature of 3 °C, and the sensors must be sufficiently accurate to resolve this difference. A low-accuracy temperature sensor on the apparatus would also be useful to correct for changes in the Zerodur length with changing temperature.

For a non-ideal compressible cavity that changes length from  $l_i$  under vacuum to  $l_f$  under pressure, equation (14) is replaced by

$$n - 1 = \frac{f_i - f_f + \Delta m(\text{fsr})}{f_f} + n \left( \frac{l_i - l_f}{l_i} \right) \quad (15)$$

where the correction factor,  $n(l_i - l_f)/l_i$ , can for our current purposes be evaluated sufficiently well using  $n = 1$ . This correction factor can be measured using helium, and subsequently the correction factor can be applied to the measurement of other gases. The correction is critical to the success of the measurement; as mentioned previously, we cannot calculate reliably the change in length of our cavities from known material properties if uncertainties below  $\approx 4 \times 10^{-8}$  are required. We must rely on the validity of calculated values for the helium refractive index in order to quantify the cavity distortions. To be very explicit about the correction procedure, we can rewrite (15) as

$$n - 1 = \frac{F}{f_f} + c(p) \quad (16)$$

where  $c(p)$  is a pressure-dependent correction factor and, speaking somewhat loosely,  $F$  is the total frequency change including the effect of mode hops:

$$F = f_i - f_f + \Delta m(\text{fsr}) \quad (17)$$

$$c(p) = n \left( \frac{l_i - l_f}{l_i} \right). \quad (18)$$

The correction  $c(p)$  is evaluated from the theoretical refractivity of helium,  $(n - 1)_{\text{He}}$ , and from frequency measurements with helium in the cavity:

$$c(p) = (n - 1)_{\text{He}} - \left\{ \frac{F}{f_f} \right\}_{\text{He}}. \quad (19)$$

The refractivity of any other gas  $X$  is then found by filling the cavity with  $X$ , measuring  $F/f_f$ , and evaluating

$$(n - 1)_X = \left\{ \frac{F}{f_f} \right\}_X + c(p) \quad (20)$$

where the parameters in (19) and (20) must all be evaluated at the same gas pressure. We have thus far described  $c(p)$  as a correction to account for length variations in the cavity, but this interpretation of  $c(p)$  is not strictly required for the validity of the method. The critical assumption is simply that, whatever the detailed origin of  $c(p)$ , it must be a function of pressure only (not of gas species). We find that  $c(p)$  is a linear function of pressure.

Equations (14) and (15) require good knowledge of the free spectral range under vacuum, which is fundamentally important because it provides a measure of the cavity length,  $l$ . The free spectral range can be measured by locking one laser to one longitudinal cavity mode and the second laser to a nearby mode of the same cavity. (The lasers are modulated at different frequencies so that the two signals do not interfere in the lock-in amplifiers.) The frequency difference between the two lasers determines the free spectral range. Since the free spectral range is multiplied by  $\Delta m$  (where  $\Delta m$  is 80 or

more), the measurement of this frequency difference is much more critical than is the measurement of  $f_i - f_r$ . Spurious reflections of the laser from surfaces external to the cavity, quasi-degeneracy of resonator modes coupled with poor mode matching, electronic offsets, or several other effects can cause the lock-points of the two lasers to shift away from the centres of the cavity resonances, disturbing the measurement of the free spectral range. To check for such effects, we can lock the diode laser first at a higher frequency than that of the gas laser and then at a lower frequency, or we can lock first to an adjacent mode and then to a mode separated by two or three orders from the gas laser. This will uncover most sources of error in the measurement, but changes in the mirror reflective phase shift as a function of frequency will give rise to an error that cannot be detected because it is very nearly a linear function of frequency for a typical dielectric mirror close to the centre of its reflection band. The frequency dependence of the phase shifts will perturb the apparent free spectral range away from the ideal value of  $c/2l$ . The frequency dependence of the phase shift can be calculated if the mirror parameters are sufficiently well known, or it can be determined from transmission measurements [25]. We know that our mirrors have a special SiO<sub>2</sub> overcoat on top of a TiO<sub>2</sub>/SiO<sub>2</sub> quarter wave stack. The detailed parameters are not known well enough to calculate the phase shift with confidence, but we suspect that the resulting error in the free spectral range will contribute an error of the order of a few parts in 10<sup>9</sup> when using the short cavity to measure the refractive index of nitrogen at atmospheric pressure. This error scales inversely with cavity length, and so it is expected to be negligibly small for our long cavity.

#### 4. Expected sources of uncertainty in measuring refractive index

The uncertainty of our device is ultimately limited by the theoretical calculations and uncertainty in the Boltzmann constant, but practical experimental considerations are currently much more important. When we use our refractometer to measure the refractive index of a gas such as air or nitrogen, we believe that the primary sources of error are as described below:

(1) The largest source of uncertainty is measurement of the environment during the helium calibration. A 7 Pa standard uncertainty for pressure and a 0.015 °C standard uncertainty for temperature measurement give rise to a combined standard uncertainty for the refractive index of helium at atmospheric pressure of  $2.8 \times 10^{-9}$ . This will be the uncertainty in the correction term of (16).

(2) A comparably large uncertainty arises in the determination of the free spectral range. We estimate the standard uncertainty as 3 kHz for the long cavity, based on the consistency of measurements made with the diode laser locked to one side or the other of the gas laser. This uncertainty is also consistent with observed differences in measured refractive index when using the long and short cavities. The resulting uncertainty for measuring the refractive index of nitrogen at atmospheric pressure is  $2.5 \times 10^{-9}$ . For the short cavity, this uncertainty increases to about  $3.5 \times 10^{-9}$  because of the mirror phase shifts.

(3) In our current system there are uncertainties of about  $2 \times 10^{-9}$  as a consequence of transients and outgassing, as discussed in the next section.

(4) Contamination of the helium might be a problem. In addition to the contamination from outgassing mentioned above, there is a possibility that our helium bottle is not pure as delivered from the factory. The manufacturer<sup>3</sup> claims a purity of 99.9999% for their helium. The remaining contaminants might increase the apparent refractive index at atmospheric pressure by about  $3 \times 10^{-10}$ , which is not important at our current level of measurement. If a lower uncertainty were required in the future, a chemical analysis of the residual contaminants should make it possible to correct for at least part of this  $3 \times 10^{-10}$  residual error.

(5) As already discussed, the uncertainty in theoretical calculations and in the Boltzmann constant contributes an uncertainty of  $8 \times 10^{-11}$ .

(6) Uncertainties in the frequency measurements (the absolute value of  $f_r$  and the difference  $f_i - f_r$ ) contribute negligibly (order of  $10^{-11}$ ) to the uncertainty in refractive index.

(7) One might imagine additional sources of error, such as changes in the mirror coatings due to adsorption of gas when the cavity is filled. We have seen possible evidence of such effects when the gas is water vapour or moist air [1] but no measurable effect for helium or nitrogen. This type of end-effect is physically independent of the cavity length and becomes less important relative to the refractive index as the cavity length increases; consequently, end-effects give rise to errors in the measured refractive index that scale inversely as cavity length. These errors can be studied by comparing results from our two cavities, as discussed in section 6. Assuming this inverse scaling with length, the results of section 6 suggest that these errors might be as large as a few parts in 10<sup>9</sup> for the short cavity but should be well under 1 part in 10<sup>9</sup> for the long cavity.

(8) Helium penetration of the bulk spacer material might also be possible. This would not show up as an end-effect. Unlike quartz, Zerodur is not very permeable to helium, and consequently there is no particular reason to anticipate problems in this regard, but it is difficult to rule out such effects with certainty. If helium were penetrating the Zerodur and modifying its length, one might imagine that we would see unusual behaviour as we go from a helium environment at atmospheric pressure to vacuum. We have not seen any such effects that could be attributed to slow helium outgassing from the Zerodur.

For the long cavity, all these sources of uncertainty yield a combined standard uncertainty of  $4.3 \times 10^{-9}$ , or an expanded uncertainty of  $9 \times 10^{-9}$  (with coverage factor  $k = 2$ ). For the short cavity, the expanded uncertainty is only slightly larger, about  $1 \times 10^{-8}$ . The uncertainty would be somewhat larger when measuring moist air with the short cavity, as discussed in [1].

<sup>3</sup> The helium and nitrogen were purchased from Scott Specialty Gases (see footnote 2). Primary contaminants of the analytical grade (99.9999%) helium are N<sub>2</sub> and O<sub>2</sub>. The primary contaminants of the 99.9993% pure N<sub>2</sub> gas were claimed to be O<sub>2</sub> and water vapour.

## 5. Nitrogen measurements

As a proof-of-principle, we have used our apparatus to measure the refractive index of nitrogen. We first measure the frequency change of the FPI cavity when it is filled with helium to determine the correction factor and then fill it with nitrogen or some other gas of interest.

Outgassing and transients are a potential source of error, as has been discussed in detail in [1]. After filling the cavity, it can take several hours for the gas temperature to reach its equilibrium value. During this period of time there are large gradients in the gas temperature within the chamber, and the average temperature measurements are probably not reliable. Furthermore, the chamber and associated vacuum lines are continuously outgassing (particularly if water vapour was recently in the chamber). To analyse the data properly, it may be necessary to (a) wait several hours for the system to reach thermal equilibrium and (b) measure changes in pressure and refractive index for several additional hours in order to characterize the effects of outgassing. An extrapolation procedure is then used to correct for outgassing. The correction is a bit uncertain, and we believe that this is the primary limitation on the short-term repeatability of our results, which is about 2 parts in  $10^9$ .

We carried out two sets of measurements of the refractive index of nitrogen. The first set was at pressures ranging from 105 kPa to 109 kPa and a temperature of 19.97 °C. The second set was at lower pressure—97 kPa to 101 kPa—and a temperature of 23.4 °C. With appropriate corrections for non-ideal gas behaviour, we can compare our two sets of results for the refractive index of  $N_2$  with each other and with previous measurements by other investigators. We find that our two sets of data are offset relative to each other. If both sets of data are analysed using the same helium correction, they differ from each other by about 3 parts in  $10^9$ . A change in the measured correction between the first and second set increases the offset to 5 parts in  $10^9$ . This provides a measure of the long-term repeatability of the system, including possible consequences of several improvements in the apparatus that were made during the interval between the first and second data sets.

From our measurements, plus known values of the virial coefficients  $B(T)$  [15] and  $B_R$  [10], we can determine the molar refractivity of nitrogen and compare this result with previous measurements. The uncertainty in molar refractivity is much greater than the actual uncertainty in our measured refractivity because determining the molar refractivity requires measurement of the temperature and pressure of nitrogen gas. Based on all our measurements, our best estimate of the molar refractivity at 633 nm is  $4.4454(7) \text{ cm}^3 \text{ mol}^{-1}$ , where the expanded ( $k = 2$ ) uncertainty ( $0.0007 \text{ cm}^3 \text{ mol}^{-1}$ ) arises primarily from the measurement of the pressure and temperature of the nitrogen gas. We are aware of four previous measurements of the molar refractivity that claim a low uncertainty. Our result is consistent with Birch's [11] value of  $4.4457(8) \text{ cm}^3 \text{ mol}^{-1}$  and is in slightly better agreement with Hou and Thalmann's [26] value of  $4.4456(6)$  or Montixi's [27] result of  $4.4454(5) \text{ cm}^3 \text{ mol}^{-1}$ . However, it is at best only marginally consistent with Achtermann's value [10] of  $4.4464(5) \text{ cm}^3 \text{ mol}^{-1}$ . If we average all four previous results for the molar refractivity, our value is lower by

$0.00037 \text{ cm}^3 \text{ mol}^{-1}$ , which is equivalent to an error of  $2 \times 10^{-8}$  in terms of the refractive index of nitrogen at atmospheric pressure. This is within our expected uncertainty.

## 6. Additional tests of the system

We can learn a great deal about the ultimate capability of our method by comparing results from our two systems (long cavity + gas laser compared with short cavity + diode laser). If we use the two systems to measure the refractive index of a common gas sample simultaneously, we can characterize accurately many sources of error that would otherwise be masked by uncertainties in our pressure and temperature measurement. For example, this test will uncover errors in the free spectral range measurement or possible end-effects (see #7 in section 4) that may be difficult to quantify using other techniques. The test thus provides an indication of the ultimate accuracy that we might hope to achieve if we had very good environmental measurement.

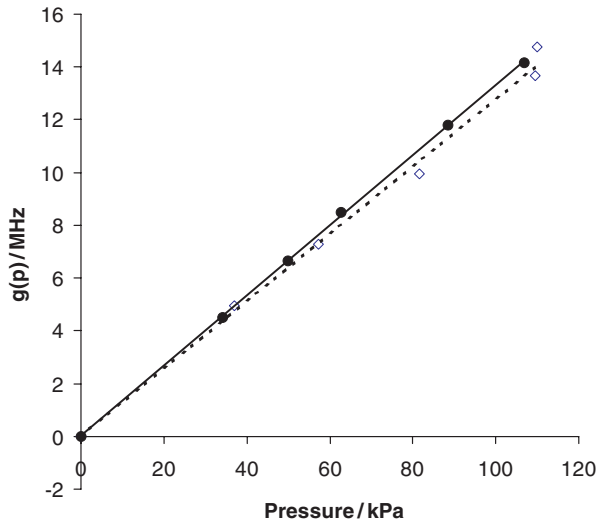
The comparison between the two systems is particularly useful because one cavity is nearly five times as long as the other. Effects associated with the cavity ends, such as certain pressure-induced distortions, gas adsorption in the coatings, or mirror phase shifts, will have five times greater effects in the short cavity than in the long cavity and hence should be easily observable.

As discussed below, a change in refractive index should ideally change the frequencies of our long and short cavities by essentially identical amounts (after correction for mode hops). It is easy to measure the difference frequency between the two cavities; it is equal to the frequency of the heterodyne beat when the two laser beams are combined on a photodetector. The frequency difference should be constant. Any observed variation thus provides a sensitive indicator of many sources of error. Below we derive the expected behaviour of the measured beat frequency as would be predicted from equations (16)–(20).

Looking back to (16) (i.e.  $n - 1 = F/f_f + c(p)$ ), it may be noted that, at a given temperature and pressure,  $F/f_f$  will be the same for both our cavities if the correction factor  $c$  is the same for both. The correction factors for the two cavities would be identical if  $c$  arises from simple homogeneous compressibility of the cavities. (The two Zerodur spacers were cut from the same Zerodur rod and should have identical material properties.) Hence we might expect that  $F/f_f$  should be identical for the two cavities. If we make the approximation that  $f_f$  in the denominator of equation (16) is constant, then the frequency change  $F$  should be the same for the two cavities. (Variations in  $f_f$  are not entirely negligible for the short cavity filled with nitrogen; the approximation may lead to errors in the following analysis that are on the edge of what might be observed experimentally.) With this approximation, the constancy of  $F/f_f$  is equivalent to saying that we expect  $g(p) = 0$ , where  $g(p)$  is a measure of how the frequency changes in the two cavities fail to track each other correctly as a function of pressure,  $p$ :

$$g(p) \equiv F_{\text{Long}} - F_{\text{Short}} = \{f_i - f_f + \Delta m(\text{fsr})\}_{\text{Long}} - \{f_i - f_f + \Delta m(\text{fsr})\}_{\text{Short}} \stackrel{?}{=} 0. \quad (21)$$





**Figure 2.**  $g(p)$  for He (●) and N<sub>2</sub> (◇). The solid line is a linear fit to the helium data, and the dashed line is a fit to N<sub>2</sub>.

In reality,  $g(p)$  is a non-zero linear function of pressure, as can be seen in figure 2; it varies by about 14 MHz, which corresponds to a potential error in the refractive index of  $3 \times 10^{-8}$  if it were not corrected. We suspect that the non-zero result for  $g(p)$  is probably a consequence of pressure-related distortions at the ends of the cavities [1]. Although this behaviour was unexpected, it should still be corrected through the helium calibration and should not affect our final answer for the refractive index of nitrogen. However, the non-ideal behaviour must be the same for helium and for nitrogen if the calibration procedure is to work properly.

From (19) and (20), it follows that if both cavities are to give the same answer for the refractive index, then it must be true that

$$\left\{ \frac{F_X - F_{\text{He}}}{f_t} \right\}_{\text{Short}} = \left\{ \frac{F_X - F_{\text{He}}}{f_t} \right\}_{\text{Long}} \quad (22)$$

which, again approximating  $f_t$  as constant, may be rearranged to give

$$g(p)_{\text{He}} = g(p)_X. \quad (23)$$

In short, the statement that the two cavities give the same answer for the refractive index of nitrogen is equivalent to requiring the equality of  $g(p)$  for helium and nitrogen. It can be seen from figure 2 that the nitrogen results are about 0.6 MHz below helium at atmospheric pressure; this corresponds to a disagreement in the measured refractive index of only  $1.3 \times 10^{-9}$ . It is likely that this excellent agreement is somewhat fortuitous. If we could reliably compensate for the effect of mirror phase shifts on the measurement of the free spectral range, it would most likely shift the results so as to increase the disagreement to a few megahertz. The resulting discrepancy would still be consistent with our uncertainty budget as discussed in section 4.

We should also note that the data of figure 2 have been corrected to account for measured temperature gradients between the two cavities, ranging from 4 mK up to 9 mK. (The comparison is insensitive to absolute temperature but does depend on gradients.) The nitrogen data lie well above

the helium results before correction but slightly below helium after correction. At the very most we might expect an error of 2 mK in the measurement of gradients less than 10 mK, and this could shift the nitrogen results by  $\pm 0.8$  MHz at atmospheric pressure. When larger temperature gradients are present, we find that we cannot reliably correct our results. Most likely the temperature is not sampled at enough points within the long cavity to characterize the average temperature accurately over the full length when the gradients are large.

## 7. Conclusions

When using our FPI to measure refractive index, we find that the pressure response of the cavity must be calibrated in order to achieve good results. This calibration is possible because *ab initio* calculations for helium can provide a known refractivity as a function of pressure, and the procedure is practical because the low refractivity of helium puts minimal requirements on the barometer uncertainty.

We claim currently an expanded ( $k = 2$ ) uncertainty for refractive index measurement that is slightly less than  $1 \times 10^{-8}$ . We have seen that our two systems agree with each other within a few parts in  $10^9$ , where the residual disagreement is plausibly understood in terms of known error sources, and therefore it may be hoped that modest improvements in our instrumentation and our vacuum system would reduce the uncertainties in refractive index measurement to a few parts in  $10^9$ . With more substantial additional effort one might hope to achieve uncertainties of the order of  $10^{-10}$ , where most of the required improvements would be straightforward albeit difficult: (a) The pressure can be known with 0.5 Pa expanded uncertainty using a calibrated gauge with good stability, such as a deadweight piston gauge. (b) Better thermal management can reduce thermal gradients to the millikelvin level and allow temperature measurement with millikelvin or even sub-millikelvin uncertainty using a calibrated standard platinum resistance thermometer. (c) Residual helium impurities can be quantified and their refractive index corrected to better than  $10^{-10}$ . (d) Outgassing in our apparatus could be easily reduced with better vacuum practice. (e) With a higher finesse cavity it should be possible to improve our free spectral range measurement by at least an order of magnitude, assuming that mirror phase shifts can be quantified and corrected. (Alternatively, a careful mechanical measurement of the cavity length might be used in place of the free spectral range measurement.) If these improvements were made, the primary source of uncertainty would be in the pressure measurement; the quoted uncertainty (0.5 Pa) is based on the best calibration capability of the National Institute of Standards and Technology, which is currently the lowest calibration uncertainty available from any national measurement institute in the world. The 0.5 Pa uncertainty for helium near atmospheric pressure would give an expanded uncertainty of  $1.6 \times 10^{-10}$  in our final result, about the same as the current overall theoretical uncertainty as given at the end of section 2.

The limiting role played by the pressure measurement suggests that refractive index measurements can be used to infer pressure with very high resolution. (To be more precise, refractive index measurements can be used to infer density [28], from which either pressure or temperature can be

determined if the other variable is known.) We can easily track pressure variations of 0.1 Pa or less in nitrogen at atmospheric pressure, comparable with the resolution of deadweight piston gauges, and this resolution would be increased if we used a higher-finesse cavity. High precision is useful, for example, to check linearity and hysteresis of a pressure transducer. The long-term stability of the Fabry–Perot, of the order of  $1/10^7$  per year, is better than the long-term stability of most deadweight piston gauges, and the stability might be improved further by using a different material for the FPI spacer. Therefore, an FPI can be used as a very good transfer standard for pressure, as has been done by Achtermann and Rogener [29]. With a refractometer of different design (a truly absolute refractometer), one might also use helium refractive index measurements as an absolute standard of pressure, just as Moldover [30] infers pressure from measurements of the helium dielectric constant.

One other important source of error in practical application of the refractometer has not yet been discussed: large errors in an interferometric measurement can occur if the air in the interferometer's measurement path is at a different temperature, pressure, or humidity from the air in the refractometer. At a minimum it may be necessary to measure and correct for temperature gradients in order to avoid these errors. It is also possible to carry out interferometric measurements directly in a helium atmosphere, and the theoretical refractive index as calculated here provides a much lower uncertainty than is available when working in air and calculating the refractive index from the measured pressure, temperature, and humidity. The effects of pressure and temperature measurement errors are reduced by a factor of 8 when using helium, and temperature gradients between the measurement path and the sensors are of much less concern than when working in air.

### Acknowledgments

We would like to thank Grzegorz Lach, Bogumil Jeziorski, and Krzysztof Szalewicz for making their results available prior to publication. Thanks to Krzysztof Szalewicz and Richard Drachman for illuminating some of the theoretical issues for us.

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