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Cell-based refractometer for pascal realization

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Abstract

We describe a method for determining the density of helium via measurements of optical refractivity. In combination with the equation of state, this allows realization of the pascal. Our apparatus is based on the integration of a gas triple-cell into a quasi-monolithic heterodyne interferometer: the stability of the interferometer is ± 50 pm over 10 h. We claim the contribution of cell window thinning to pathlength uncertainty can be canceled within an uncertainty of 0.37 fm/Pa per window pass, of which for our 25 cm cell length corresponds to a fractional error of 9.3×10^{-6} in the measure of helium refractivity. We report the ratio

$(n - 1)_{\text{N}_2} / (n - 1)_{\text{He}} = 8.570354(13)$ at $p = 367.420(4)$ kPa, $T = 293.1529(13)$ K and $\lambda = 632.9908(6)$ nm, which can be used to calibrate less-accurate refractometers. By measuring helium refractivity at known temperature and pressure, we determined the Boltzmann constant with standard uncertainty $k_B = 1.380652(17) \times 10^{-23}$ JK⁻¹.

OCIS codes

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The virial equation of state for a real gas is written as

$$p = k_B T \left(\rho + B_\rho \rho^2 + C_\rho \rho^3 + \dots \right), \quad (1)$$

where p is pressure, k_B is the Boltzmann constant, T is thermodynamic temperature, and ρ is the number density. The density virial coefficients B_ρ and C_ρ take into account the nonlinearity of pressure with density and for helium can be calculated from first principles [1]. The number density can be determined by combining experimental measurements of gas refractivity $n - 1$ with theoretical calculations that predict the dependence of ρ on $n - 1$ through the Lorentz–Lorenz equation, rearranged as

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$$\rho = \frac{2}{3A_R}(n-1) + \frac{A_R+4B_R}{9A_R^2}(n-1)^2 + \frac{4(A_R^4+4B_R-A_R^3B_R+2A_R C_R)}{27A_R^5}(n-1)^3 + \dots, \quad (2)$$

where the refractivity virial coefficients $A_R = \frac{4\pi}{3}(\alpha + \chi)$, B_R and C_R depend polarizability α and diamagnetic susceptibility χ , and for helium can be calculated from first-principles [2]. The number density in Eq. (2), deduced by helium refractometry, could be used in Eq. (1) in one of several ways: (a) a measurement of p together with the CODATA [3] value for k_B to realize the kelvin, (b) a measurement of T together with k_B to realize the pascal, or (c) measurements of T and p for a determination of k_B [4,5]. In 2007, Schmidt *et al.* [6] measured the microwave refractivity of helium with 9.1×10^{-6} relative standard uncertainty; theoretical calculations of the static polarizability of helium linked the measured microwave refractivity to gas density. This Letter describes a measurement of the optical refractivity of helium with 12.5×10^{-6} relative standard uncertainty. These measurements were used with Eq. (2) and Eq. (1) to determine the Boltzmann constant, and although our performance is not competitive with higher-accuracy measurements reported to date using alternative means [7], our measurement of helium refractivity (optical) is at least 40 times more accurate than previous reports [8,9]. We also use our apparatus as a primary pressure standard to measure the ratio of nitrogen-to-helium refractivity: such a ratio will find application in practical standards of pressure that employ less-accurate refractometers.

Our apparatus in Fig. 1 integrates a gas triple-cell into a quad-pass differential heterodyne interferometer; we call the device a monolithic interferometer for refractometry (MIRE). In the typical mode of operation, all cells are pumped to vacuum, and the phase difference in the interferometer is measured. Then the center cell is filled with gas while the two outer cells are kept at vacuum, and the phase difference in the interferometer is measured once more; by accounting for the change in fringe order plus the measured change in phase difference, the refractivity of the gas is obtained. The largest systematic error in the measurement is geometric thinning, and stress-induced changes in the refractive index of the window as pressure inside the cell increases: this end effect represents a fractional error in helium refractivity of $580 \times 10^{-6} \cdot p$ in a 25 cm cell. Our approach to cancel this error to $9.8 \times 10^{-6} \cdot p$ consists of performing refractivity measurements in triple-cells of different lengths but with almost identical bore diameters, window thickness, material properties, and beam incidence.

MIRE is based on a Tanaka-style interferometer [10] with three interchangeable gas triple-cells, and is influenced by the work of Weichert *et al.* [11]. The building of MIRE was previously described [12]. Succinctly, the interferometer has two notable features: (a) apart from the fiber launch ferrules, all optics are silicate-bonded, either to the baseplate or face-bonded to one another, and (b) the four beams through the triple-cell are parallel to the baseplate polished surface and straightedge within $\pm 85 \mu\text{rad}$ (i.e., beams parallel to two planes and, thus, parallel to one another). The former feature provides ultralow drift during a refractivity measurement, typically less than 100 pm over 10 h. The latter feature is key to ensuring similar beam incidence through triple-cells of different lengths (and also

reproducible positioning): we are confident that beam position on a pair of windows is the same within 100 μm , independent of triple-cell length. The gas triple-cells are made of borosilicate crown glass, and consist of a spacer with three bore-holes and with two windows silicate-bonded to either end. The triple-cells are 254 mm, 134 mm, and 18 mm long, with a (75×25) mm cross-section; at the point of window contact, the bores are (19.15 ± 0.05) mm diameter for the short cell and (19.04 ± 0.03) mm diameter for the medium and long cells. An end-face photograph of the short triple-cell is shown in Fig. 1. Each borehole has an inlet and outlet, and gas lines with O-ring seals are clamped onto the triple-cell body. One end of the triple-cell spacer is tilted at 1.5 mrad relative to the center axis, and the opposite end is tilted at 1.0 mrad relative to this. The tilts are large enough to avert deleterious reflections but small enough to infer accurate dimensional measurement of the triple-cell length at the point of beam incidence. The 2.5 mrad wedge between the end faces is similar within 0.1 mrad for all three triple-cells. The windows are all cut from the same piece of glass, parallel to 50 μrad , and have a 0.1% reflective coating masked to overlap the three bores; the thickness of the windows is nominally 3.35 mm: the short and long triple-cells have 0.1 μm uniformity in window thickness, whereas the medium cell has windows 10 μm thicker.

MIRE sits in a thermal enclosure and vacuum system, stabilized to 1 mK and pumped to lower than 10 mPa, and the drift in our interferometer is typically less than 100 pm over 10 h, as shown in Fig. 2. These data were acquired without a triple-cell in place: the interferometer pathlength, Jamin beamsplitter (jbs) to final polarizing beamsplitter (pbs) in Fig. 1, is about 1.5 m. During refractivity measurements with a triple-cell in place, we typically observe daily fluctuations of 50 pm in the “zero” pathlength (i.e., all three cells pumped to vacuum), and total variation over 10 d less than 200 pm. This stability performance is chiefly from its copropagating path-lengths being in close proximity. It is worth noting that a 100 pm drift in the pathlength through a quad-pass 25 cm triple-cell would represent a fractional error of 1.2×10^{-6} at 300 kPa in the measurement of helium refractivity. The stability of the phasemeter, plotted as spectral density in Fig. 2(b), was evaluated by feeding a split 1.9 MHz synthesizer signal to the measurement and reference inputs.

Gas refractivity in a triple-cell can be calculated from

$$n - 1 = \frac{(2\pi N + \Delta\phi) \cdot \lambda}{8\pi L} - \frac{2d_w \cdot p}{L}, \quad (3)$$

where the interferometric phase change ϕ is what is actually measured during a change in gas pressure; the integer change of fringe N is readily ascertained through knowledge of the change in gas pressure at the known temperature. The two terms vacuum-wavelength λ and triple-cell length L are measured beforehand by other means. The last term $d_w \cdot p$ is the change in the optical pathlength of the window when the cell is filled with gas and is proportional to pressure. It is useful to write the refractivity as a relative measurement between two triple-cells of different lengths $n - 1 = \Phi \cdot \lambda / (8\pi L)$. The main reason to do this is that we treat d_w as an end effect, and if d_w is identical for all triple-cells, the term

cancels in a relative measurement: how well this term cancels is the largest uncertainty in our measurement and is discussed below. Another reason to write the refractivity as a relative measurement between triple-cells of different lengths is that we can measure the difference between triple-cell lengths L three times more accurately than the absolute length of any triple-cell; furthermore, only differences in window bond and coating thicknesses contribute to L .

When MIRE was used to measure helium refractivity at a known pressure and temperature, we determined the Boltzmann constant in Eq. (1) with a relative standard uncertainty listed in Table 1. Our experimental limitations in measuring helium refractivity are more than 80 times larger than current uncertainties in the theoretical calculations of gas properties done by others. Uncertainty in the interferometric phase change Φ comes from a combination of interferometer stability (100 pm), periodic nonlinearity (<100 pm), and phasemeter accuracy (50 pm). (We have observed consistent values for ϕ during simultaneous measurements with phasemeters from different manufacturers.) Vacuum-wavelength λ was measured by comparing the interferometer laser to an iodine-stabilized laser; 10 MHz is a conservative stability estimate for our metrology laser. Relative cell length L was measured by a coordinate-measuring machine with 43 nm standard uncertainty, but there are added uncertainties arising from surface form (35 nm), end-face tilt and beam deviation (100 nm), and silicate-bond thickness (50 nm). (We have measured thicknesses of sample bonds with a scanning electron microscope as 100 nm, which is in close agreement with other reports for the same bonding-solution recipe [15]; the same recipe was used for windows on all triple-cells.) We note that uncertainty in the coefficient of thermal expansion of crown glass is the main reason why we measure refractivity at 20°C, the same temperature at which the triple-cell lengths were determined.

The term $d_w \cdot p = w_f \cdot (n_f - 1) + w_i \cdot (1 - n_i)$ takes into account changes in optical pathlength, per window per pass, caused by window distortion and stress; the term depends on the initial w_i and final w_f geometric thickness of the window, and the initial n_i and final n_f refractive index of the glass resulting from a change in pressure inside the cell. In our experiment, we observed $d_w = -23.8$ fm/Pa, and our model of cell window effects predicts a change in optical pathlength of $d_w = -24.8$ fm/Pa, which is within 6% of what is observed. (For the case of pressure increasing inside a cell, we observe/predict a decrease in the geometric thickness of the window and an overall decrease in optical pathlength through the window. Our model also takes into account what happens at the window as the beams pass through the outer cells held at vacuum, which has effects 87% smaller than what happens at the inner cell where pressure is changing. If we fill the outer cells and hold the inner cell at vacuum, our model predicts a 0.50 fm/Pa increase in d_w ; experimentally we observed a 0.48 fm/Pa increase.) Our treatment of the change in window pathlength follows that of Shelton [16], where we use finite-element analysis to calculate the change in geometric thickness in response to pressure $w_f - w_i = -37.3$ fm/Pa, and our estimate of the change in refractive index comes from literature values for the photoelastic coefficient of crown glass [17], which is polarization- and stress-dependent; our finite-element model also tells us the tensile (1.9 Pa/Pa) and compressive (-0.5 Pa/Pa) stresses on the windows at the point of beam transmission that are used to calculate the change in refractive index $n_f - n_i = -1.33 \times 10^{-12}$ /Pa. This approach of Shelton differs from that of Birch *et al.* [18], because the latter

made the assumption that a change in fractional length of the window was equal to a fractional change in glass density (and hence refractive index, through the Lorentz–Lorenz equation): application of the Birch *et al.* approach to our case yields $d_w = +3.4$ fm/Pa; i.e., seven times smaller and opposite sign compared to what we observe/predict. We must note that, as aforementioned, our experiment is designed such that the term d_w cancels from the measurement of gas refractivity: we only employ our model of d_w (which relies on finite-element analysis) insofar as triple-cell and window geometries lack similarity, and small adjustments to d_w for each triple-cell need to be made. Two adjustments to d_w are used: a -79 am/Pa adjustment to the short triple-cell because its bore diameter is $110\text{ }\mu\text{m}$ larger than the other two triple-cells, and a $+71$ am/Pa adjustment to the medium triple-cell because its windows are $10\text{ }\mu\text{m}$ thicker than the other two triple-cells. These adjustments are based on bore and window geometries that were measured before the windows were bonded to the cell. We consider the largest uncertainty on d_w to come from mismatch of beam incidence: the four beams through the cells are parallel to $+85\text{ }\mu\text{m}$, which means beam incidence between long and short triple-cells could differ by as much as $78\text{ }\mu\text{m}$ on one window. Additionally, irreproducibility in triple-cell positioning will contribute to differing points of beam incidence. Based on a sensitivity analysis of our window pathlength model, we estimate the uncertainty on d_w to be 0.37 fm/Pa. This end effect is the largest contributor to uncertainty in our refractivity measurement; we have next-iteration designs, optimized by our window pathlength model, that reduce d_w by a factor of 3, and we are confident beam alignment could also be improved upon [12].

Gas temperature in the triple-cell was measured by thermocouples, which sensed the difference between the triple-cell (in vacuum) and the reference junction. The reference junction is a large aluminum block epoxied onto a feedthrough flange that has a thermowell on the air side. The temperature of the reference junction was measured in the thermowell by a capsule-type standard platinum resistance thermometer (SPRT). This arrangement avoids the changes in self-heating that occur in an SPRT in air versus if used in vacuum, and the 1 mm diameter of the thermocouple allowed us to measure gas temperature directly on the cell. Thus, how well we know gas temperature is a combined uncertainty of the thermocouple offset emfs and nanovoltmeter drift, SPRT calibration, and difference between ITS-90 and thermodynamic temperature [19] at 20°C ; the latter two components could be reduced by operating at the triple point of water, but accounting for the thermal expansion of our current triple-cell would require dilatometry. We note that the temperature difference between the triple-cell and reference junction was usually within 1 mK at steady state, but a 367 kPa helium fill increased glass temperature by about 45 mK , and we had to wait 4 h for the transient to settle before measuring refractivity; this process is the main driver behind our requirement on MIRE stability. We used a piston gauge to generate a known gas pressure, which had been previously compared to a primary pressure standard [20], and thus our uncertainty is a combination of the primary standard and cross-float comparison uncertainties. Last is the uncertainty due to gas impurity: we are limited by the 99.9999% purity helium that comes from standard cylinders and analysis certificates; we envisage that a next-iteration MIRE, having triple-cells made in low-thermal-expansion glass ceramic and with smaller d_w would need to purify through a liquid-helium cold-trap. In summary, with a 2:1 weighting on results from long and medium triple-cells, our determination and standard

uncertainty on the Boltzmann constant is $k_B = 1.380652(17) \times 10^{-23} \text{ JK}^{-1}$ and expressed in fractional terms differs from CODATA [3] by $(2.2 \pm 12.5) \times 10^{-6}$.

To conclude, in the context of the proposed revision to the SI for 2018, the Boltzmann constant will be exact; at that point in time, a refractometer such as the one reported here could be used to realize the pascal, when pressure is chosen as the unknown in Eq. (1), and the thermodynamic temperature of helium is measured. Agreement between the refractometer p_{MIRE} ($\text{Pa} = \text{J/m}^3$, using the CODATA value for k_B) and the piston gauge p_{PG} ($\text{Pa} = \text{N/m}^2$) is shown in Fig. 3, either filling the inner or outer cells of long and medium triple-cells with helium. From a practical perspective, however, we would advocate Fabry–Perot refractometry of nitrogen gas as a standard of pressure: the simplicity of the device reported in Ref. [21], and its much higher precision and range are important practical advantages for pressure metrology, as are the wide availability and lower cost of research purity nitrogen, and its relative insensitivity to typical contaminants. To use this method of pressure measurement requires knowledge of nitrogen refractivity as a function of pressure. This relationship can be measured using our triple-cell. Our result is best expressed as a ratio of nitrogen-to-helium refractivity when both are at the same temperature and pressure: we found $(n - 1)_{\text{N}_2} / (n - 1)_{\text{He}} = 8.570354(13)$ at $p = 367.420(4) \text{ kPa}$, $T = 293.1529(13) \text{ K}$ and $\lambda = 632.9908(6) \text{ nm}$. Since the refractivity of helium is known from calculation, the nitrogen refractivity is implicitly determined by the ratio. The ratio is nearly independent of small changes in temperature and pressure, but for larger changes it is necessary to have accurate knowledge of virial coefficients. Knowledge of the nitrogen and helium refractivities would allow correction of distortion errors in the Fabry–Perot refractometer of Ref. [21], without reference to N/m^2 , allowing the device to serve as a useful semiprimary [22] pressure standard, if the ratio of nitrogen-to-helium refractivity is known with sufficient accuracy.

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Fig. 1.

Components to make a MIRE include: stabilized helium–neon (He–Ne) laser, isolator (iso), beamsplitter (bs), acousto-optic modulator (aom), fiber coupler (fc), polarization-maintaining fiber (pm-smf), fiber launch (fl), wedge prism pair (wpp), Jamin beamsplitter (jbs), thin-film polarizer (pol), polarizing beamsplitter (pbs), mirror (m), photodetector (pd).

Fig. 2.
 (a) MIRE drift with 600 s averaging; (b) spectral density of drift in MIRE (“mire”) and phasemeter (“lia”).

Fig. 3.

Agreement between helium pressure generated by a piston gauge p_{PG} and measured by triple-cells p_{MIRE} . The error bars span $u_r(p_{MIRE})$ and are offset by 3 kPa for clarity.

Table 1

Relative Standard Uncertainty on Our Determination of the Boltzmann Constant

Quantity	$u_r(k_B) \times 10^6$	Refs.
from theory		
$A_R = 0.52025577(6) \text{ cm}^3/\text{mol}$	0.12	[2]
$B_R = -0.0542(2) \text{ cm}^6/\text{mol}^2$	0.02	[2]
$C_R = -0.71(17) \text{ cm}^9/\text{mol}^3$	0.01	[2]
$B_\rho = 11.847(1) \text{ cm}^3/\text{mol}$	0.05	[1,13]
$C_\rho = 109.3(4) \text{ cm}^6/\text{mol}^2$	0.02	[13,14]
for this experiment		
$\Phi = 2.999653(7) \text{ mrad/Pa}$	2.2	
$\lambda = 632.9908(2) \text{ nm}$	0.03	
$L = 236.38641(14) \text{ mm}$	0.6	
$d_w = -23.75(37) \text{ fm/Pa}$	9.8	
$p = 367420.0(16) \text{ Pa}$	4.3	
$T = 293.1529(13) \text{ K}$	4.5	
impurity 0.0001%	4.0	
combined ($k = 1$)	12.5	