Published in final edited form as:

Rev Sci Instrum. 2016 May ; 87(5): 053113. doi:10.1063/1.4949504.

Comparison measurements of low-pressure between a laser refractometer and ultrasonic manometer

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Abstract

We have developed a new low-pressure sensor which is based on the measurement of (nitrogen) gas refractivity inside a Fabry–Perot (FP) cavity. We compare pressure determinations via this laser refractometer to that of well-established ultrasonic manometers throughout the range 100 Pa to 180 000 Pa. The refractometer demonstrates $10^{-6} \cdot p$ reproducibility for $p > 100$ Pa, and this precision outperforms a manometer. We also claim the refractometer has an expanded uncertainty of $U(p_{\text{FP}}) = [(2.0 \text{ mPa})^2 + (8.8 \times 10^{-6} \cdot p)^2]^{1/2}$, as realized through the properties of nitrogen gas; we argue that a transfer of the pascal to $p < 1$ kPa using a laser refractometer is more accurate than the current primary realization.

I. INTRODUCTION

For centuries low-pressures (1 Pa to 100 kPa) have been measured using liquid column manometers. The pressure $p = h\rho g$ in a U-tube manometer comes from a measure of the column height h , where gravity g and the fluid density ρ are well-known. The most accurate determinations of column height are done today with ultrasonic interferometer manometers (UIM), and $U(p_{\text{UIM}}) = [(6 \text{ mPa})^2 + (5.2 \times 10^{-6} \cdot p)^2]^{1/2}$ expanded uncertainties can be achieved^{1,2}. The well-established history of the approach, its accuracy, and the direct relation between pressure and column height, have all made the liquid column manometer a difficult technology to displace.

Nevertheless, there is a growing interest in alternative methods of measuring pressure, and in possible realization of the pascal through the atomic properties of gases^{3,4}. The motivation is chiefly ecological—the favored fluid for manometers is the toxin mercury—and there are a number of conventions (international and state) that limit use/release/trade of mercury (see, for example, mercuryconvention.org). In addition to environmental concerns, an alternative method of measuring pressure might overcome the technical drawbacks of manometers, among which are slowness, size, sensitivity to vibration, and limited range: NIST’s mercury manometer is 3 m tall, its 230 kg of mercury prefers to move in one direction, after settling it takes about 60 s to measure a pressure, best measurements are obtained before daily road traffic begins, and the difficulty of correcting for mercury-vapor limits its useful low-end range to a few hundred pascal.

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In the past several years we have been developing a pressure sensor that utilizes a laser refractometer and the ideal gas relation $p \propto (n - 1)k_B T$, where the pressure of a gas can be determined by a measure of the gas refractivity $n - 1$ (which is proportional to number density) and thermal energy $k_B T$. The metrology behind our technique is interferometry (and laser wavelength), which is used to measure the optical length of a Fabry–Perot (FP) cavity at vacuum and then at pressure. Similar work in the field of laser refractometry^{5–9} has been at the level of a few parts in 10^8 ; we measure nitrogen refractivity to 3×10^{-10} by keeping distortions/instabilities small through design, and correcting for the remainders using helium, whose refractivity is known from theory¹⁰. Our apparatus is small (about 30 cm^3), fast and precise (1 mPa for 1 s averaging), and can hold this precision across more than five decades of pressure. In this paper we compare pressure determinations from two separate refractometers to that of a mercury manometer. We describe the comparison tests and provide an uncertainty budget; in tandem, these elucidate the performance one might expect when using a laser refractometer to measure pressure.

II. METHOD AND RESULTS

The basis of our approach to measure pressure via gas refractivity and a dual FP cavity refractometer is outlined in Ref. 11. We form reference and measurement FP cavities by silicate-bonding two pairs of mirrors to the ends of one ultralow expansion (ULE)¹² glass spacer. A HeNe laser is dither-locked to the TEM_{00} resonance of each cavity, and the measure of these resonance frequencies (either absolute or relative to one another) tell us the optical lengths, or changes in optical length, of both cavities: optical length is nL , where n is the refractive index of the medium, and L the physical separation, between the mirrors. The reference cavity is permanently held at vacuum and serves as a reference length; the measurement cavity begins at vacuum and is then filled with gas, and its optical length changes (mostly) because of the increasing refractivity. The difference between the optical lengths of the reference cavity and gas-filled measurement cavity is a measure of the gas refractivity; our measure of pressure is proportional to gas refractivity through the Lorentz–Lorenz equation and ideal gas law. It is worth noting that for nitrogen, measuring 1 kPa of pressure to $10^{-6} \cdot p$ requires a measurement of the fractional change in optical length of the measurement cavity to better than 3 pm/m (or 0.5 pm on our 150 mm cavity length).

As a further test of the performance of this approach, we built a second laser refractometer system, with the objective of comparing two separate refractometers head-to-head against NIST manometers, which offer one of the world’s most accurate realizations of the pascal. The schematic of the test is shown in Fig. 1. While it is true that not every potential systematic error can be uncovered in a head-to-head comparison like this, some important ones are: in particular, thermometry and transfer manometry. For thermometry: a 1 mK error in gas temperature would cause an apparent $3.3 \times 10^{-6} \cdot p$ disagreement in the pressure reading from either refractometer system, and a head-to-head comparison using separate thermal systems (for temperature control and measurement) is one way to build confidence that we accurately know gas temperature. For transfer manometry: we must employ a differential capacitance diaphragm gage (CDG) in a null-configuration when comparing to the manometer to prevent the migration of mercury vapor and other contaminants to the refractometer (whose accuracy depends upon the purity of nitrogen). A null configuration

means that each side of the diaphragm is simultaneously filled with gas, so that when the UIM and refractometer reach their final pressures, the pressure differential across the CDG is nominally zero. Two separate CDGs plumbed in opposite polarity is a crosscheck against possible errors that arise when transferring the accuracy of the manometer to the refractometer. Additionally, there are some small differences in the FP cavities at the heart of each refractometer system: they are made of glass from different batches with slightly different geometries (that is, each cavity has different compressive distortion terms), and the mirrors of each are from different coating runs with reflectivities of 99.7% and 99.8% (that is, each cavity has a different mirror dispersion).

A. Gas pressure in a Fabry–Perot cavity

As described in in Ref. 11, the pressure of the gas in the dual FP cavity refractometer is measured as

$$p_{\text{FP}} = \frac{1}{c_1 - d_m - d_r} \left(\frac{\Delta f}{\nu} \right) - \frac{c_2 - c_1 d_m}{(c_1 - d_m - d_r)^3} \left(\frac{\Delta f}{\nu} \right)^2 + \frac{2(c_2 - c_1 d_m)^2 - c_3(c_1 - d_m - d_r)}{(c_1 - d_m - d_r)^5} \left(\frac{\Delta f}{\nu} \right)^3, \quad (1)$$

where $\frac{\Delta f}{\nu}$ is the effective fractional change in cavity resonance, d_m and d_r are distortion terms, caused by compressive pressure, for the measurement and reference cavities, respectively. The constants

$$c_1 = \frac{3}{2k_B T} A_R$$

$$c_2 = \frac{3}{8(k_B T)^2} (A_R^2 - 4A_R B_\rho + 4B_R) \quad (2)$$

$$c_3 = \frac{3}{16(k_B T)^3} (5A_R^3 - 4A_R^2 B_\rho + 16A_R B_\rho^2 + 4A_R B_R - 16B_\rho B_R - 8A_R C_\rho + 8C_R),$$

are defined by the refractivity virial coefficients (A_R , B_R , and C_R), the density virial coefficients (B_ρ and C_ρ), and k_B is the Boltzmann constant and T is thermodynamic temperature. The proportionality constants in (1) are fixed properties of the gas species

which fills the cavity, and it is the terms $\frac{\Delta f}{\nu}$, d_m , and d_r that are specific to each FP cavity: these terms need to be characterized before a gas pressure can successfully be determined with a refractometer.

The effective fractional change in cavity resonance is what is actually measured for a given change in pressure, and it is expressed as

$$\frac{\Delta f}{\nu} = \Delta \nu_{\text{fsr}} (1 + \varepsilon_{\alpha}) \cdot \frac{\frac{f_i - f_f}{\Delta \nu_{\text{fsr}}} + \Delta m}{f_f + \nu_f}. \quad (3)$$

To measure pressure, one starts with an initial rf beat frequency f_i between the resonances of the measurement and reference cavities (with the measurement cavity at a known pressure such as vacuum), then one fills the measurement cavity with gas and obtains a final rf beat frequency f_f between the resonances of the two cavities. Our HeNe lasers do not have enough tuning range to cover much more than a 900 Pa change in (nitrogen) pressure, so we must relock the laser to a lower resonance of the measurement cavity, when pressure increases by more than this amount, and keep track of the change in mode order m . (As a working pressure standard, the refractometer needs a method of determining m without ambiguity. Several methods are available to make this determination, but for pressures on the order of 200 kPa or less, the easiest approach is probably to employ a supporting pressure gage of modest accuracy. The ancillary gage requires only 0.2% uncertainty over this pressure range in order to unambiguously identify the order. Another minor complication occurs when measuring $p > 120$ kPa, since the compressive change in length makes it more likely than not that the laser will have to be relocked to a higher resonant mode of the reference cavity, and f_i in (3) would be adjusted to include a free-spectral range of the reference cavity.) To achieve precisions better than $10^{-6} \cdot p$ in the refractometer it is also necessary to know the absolute resonant frequency of the measurement cavity ν_f when at pressure; this is routine if using a HeNe laser and after (once-off) calibrating the vacuum resonance of the measurement cavity against a known frequency reference. The remaining two terms in (3) are the free spectral range of the measurement cavity ν_{fsr} and its mirror dispersion ε_{α} (how much the mirror reflection phase shift changes as a function of laser frequency). We measure the free spectral range as the rf beat frequency between two lasers locked to adjacent modes of the cavity (again, a once-off characterization step); the mirror dispersion comes from the coating manufacturer and if unaccounted for would contribute an error of up to $8 \times 10^{-6} \cdot p$ to a pressure measurement.

The remaining two parameters in (1) are the reference and measurement cavity distortions d_r and d_m , which are characteristic to each FP cavity-based refractometer. These distortions arise because the refractometer compresses when the measurement cavity is filled with gas. The distortions are predominantly caused by the finite bulk modulus of the glass from which the refractometer is made, and so $d_m \approx -d_r$. However, this approximation is not accurate enough, because the reference cavity has some mirror bending (in addition to bulk modulus compression), and so each distortion term needs to be determined in its own right. The distortion term d_r is determined by monitoring how the absolute resonance frequency of the reference cavity changes as the exterior of the refractometer is brought to pressure; the change in absolute resonance is measured by beating the cavity resonance against a known laser frequency reference, in our case an iodine-stabilized laser. The distortion term d_m is determined using helium: we fill the measurement cavity with helium of known pressure and

temperature and calculate the theoretical refractivity; the error between the calculated refractivity and what the refractometer measures is attributed to d_m . As an aside, it might be reasonably expected that d_r and d_m will be constant on a timescale of decades, perhaps never requiring recalibration, but this remains to be proven.

B. Uncertainty analysis

The starting point in the uncertainty analysis of a pressure measurement by laser refractometry is Eq. (1) and (2). In the top part of Tab. I we list expanded uncertainties for all parameters in these equations, and show the contribution of each parameter to the relative expanded uncertainty for a pressure determination at 100 kPa. The refractivity and density virial coefficients in Tab. I are expressed in the customary units of $\text{cm}^{3x}/\text{mol}^x$ for $x = 1, 2, 3$; for use with (1), the coefficients must be converted to units m^{3x} , by multiplying by the factor $(10^6 \cdot N_A)^{-x}$, where Avogadro's constant $N_A = 6.022\,140\,86(15) \times 10^{23} \text{ mol}^{-1}$ is from the most recent CODATA¹³. It is worth noting that the chief contributor to $U(p_{\text{FP}}) - A_R$, the first virial coefficient of nitrogen refractivity—comes from a measurement of nitrogen refractivity $n - 1 = (26\,485.28 \pm 0.3) \times 10^{-8}$ at $p = 100.0000(6) \text{ kPa}$, $T = 302.919(1) \text{ K}$ and $\lambda_{\text{vac}} = 632.9908(2) \text{ nm}$; thus, $U(p_{\text{FP}})$ at this particular pressure is entirely independent of other virial coefficients. Furthermore, since we operate at the same temperature and vacuum-wavelength, a certain cancellation of errors occurs at other pressures, leading to a complicated relationship between the uncertainty of the final result and the uncertainty of the parameters in the table. In effect, the uncertainties in the table are not truly independent quantities for several reasons, and in writing the uncertainty in the traditional form of a simple quadrature sum of a length-independent and a length-proportional term, we have ignored various complications. The stated uncertainty is therefore very slightly overestimated, but the overall effect is negligible unless future measurements significantly reduce the uncertainty of the dominant first term. Another important point is that knowledge of A_R is limited by how well nitrogen gas pressure can be measured with a manometer: if the pascal can be realized more accurately than current means, the more accurate measurements of A_R would correspondingly reduce $U(p_{\text{FP}})$. The second largest contributor to uncertainty is thermodynamic temperature: we work very close to the melting-point of gallium where thermometer calibration errors are small, because thermal stabilization is relatively easy by heating an instrument above room temperature with foil heaters (as compared to immersing the instrument in a cold bath). The disadvantage is that the expanded uncertainty of thermodynamic temperature at the gallium melting-point is 0.8 mK¹⁶: to reduce the contribution of temperature uncertainty to $U(p_{\text{FP}})$, our apparatus would have to be modified in order to work at the triple-point of water. We also mention that daily drifts in our thermal control system are on the order of 0.1 mK, and are of negligible concern since gas temperature is continuously measured during pressure runs.

The uncertainties in the characteristics of the FP cavities are about seven times smaller than current uncertainties in gas properties. The largest is how well we can correct for measurement cavity distortion d_m . We correct this distortion using helium as a standard of refractive index. The chief error in the correction is helium permeation into the glass, which changes the length of the cavity after a fill, and results in a $1 \times 10^{-6} \cdot p$ relative expanded uncertainty in d_m . There are other glasses (or glass-ceramics, such as Zerodur¹²) that have

much lower helium permeability rates than ULE, but alternative materials may come at the cost of larger compression hysteresis, dimensional drift, and/or thermal expansion. The two other most significant uncertainty components in determining d_m are the measurement of helium pressure and the purity of helium, which both contribute about $0.8 \times 10^{-6} \cdot p$. Since we must fill and measure rapidly with helium (to avoid significant changes in cavity length, aforementioned), we can not use the manometer to measure pressure, and must rely on a secondary gage with very recent calibrations against the manometer. Helium purity comes from the best that is available in gas cylinders; it is possible to purify helium at the point of use, but that requires great effort and would yield little benefit since helium purity is not the largest error source in d_m . The uncertainty in the measurement of the effective change in

fractional frequency $\frac{\Delta f}{\nu}$ is dominated by uncertainty in mirror dispersion ε_a , which we are confident of correcting to 10 %; another error arises if one wishes to avoid the necessity of an external reference laser, because ν_f in (3) is estimated from a onetime measurement of the measurement cavity resonance at vacuum, and the estimation develops error due to drift in the relative cavity lengths, corresponding to a relative error in pressure measurement of $6 \times 10^{-8}/\text{yr}$. Lastly, our uncertainty in correcting for reference cavity distortion d_r is based on a 2σ spread of many measurements across a wide range of compressive pressures (and is discussed more in the next subsection). [It is worth noting that the distortion terms d_m and d_r are related to the material properties of the glass, and, in the case of ULE, are temperature dependent at about $3.8 \times 10^{-4}/\text{K}$ around $(30 \pm 6)^\circ\text{C}$. While it is true that some cancellation of error occurs, because d_m and d_r predominantly arise due to finite bulk modulus, our refractometer exhibits a $3.5 \times 10^{-7}/\text{K}$ fractional error in pressure measurement if used at a temperature other than the one at which d_m and d_r were characterized.]

In addition to the uncertainties in the parameters of (1) and (2), there are experimental limitations, as listed in the bottom part of Tab. I. These limitations end up dominating $U(p_{\text{FP}})$ at lower pressures because they are responsible for an offset term in the refractometer (a pressure independent error). Notably absent from this list is what we had previously observed as nonlinear lengthening after a gas fill¹¹: this effect is no longer present (in either refractometer), and we attribute its cause to instabilities in the silicate-bonds from which the cavities are made, bonds which have subsequently been vacuum-baked for two months at 100°C . The largest contributor to the offset term is outgassing, which compromises the purity of the nitrogen fill gas. Our chamber and fittings are entirely o-rings and we would expect to see reductions in outgassing by converting to metal gaskets (indeed, 80% of the total o-ring surface area is in the lid of the chamber, so changing the chamber alone to metal gaskets would significantly improve matters). The uncertainty contribution of the second largest offset term—lock offsets—can be reduced by using dual FP cavities of higher finesse (higher mirror reflectivity), or through more careful attention to sources of locking error such as residual amplitude modulation. However, even without mitigating the problem of outgassing or lock offsets, our stated uncertainty in Tab. I would imply a transfer of the pascal to pressures below 1 kPa with a refractometer is more accurate than a primary realization with a manometer.

C. Comparison tests

We performed a series of tests over about two months that compared the two separate refractometer systems to NIST's ultrasonic manometer for pressures up to 180 kPa. The results are shown in Fig. 2(a), where the fractional disagreement between pressure measured by the refractometer and manometer is plotted as a function of pressure. When comparing the refractometer to the manometer, there are several additional uncertainties which contribute to the measurement and are not listed in Tab. I. The first and most significant is transfer-manometry. Since the accuracy of the refractometer depends upon gas purity, we must employ a differential capacitance diaphragm gage (CDG) in a null-configuration to separate the refractometer from the manometer. Our study of the CDGs showed that they introduce an offset term of up to 6 mPa, caused by irreproducibility of the zero (that is, the reading when high-vacuum is on both sides of the CDG); in addition, the null-configuration requires simultaneous filing of the refractometer and manometer, while keeping a low pressure differential across the diaphragm so as to prevent a strain-induced error in the CDG, and we attribute a $2 \times 10^{-6} \cdot p$ expanded uncertainty caused by this procedure. Since the refractometer and manometer operate at different temperatures (29.767 °C and 23.0 °C, respectively), there is a nonlinear pressure correction owing to thermal transpiration which is approximately 15 mPa at 100 Pa, but the uncertainty in this correction is less than 10 %. Another factor influencing the comparison is data synchronization: our manometer has an unpredictable acquisition time of about 15 s, and during this time we take an average of many 0.4 s readings from the refractometer (frequency counters) and CDG, but the lack of perfect overlap between the three measurements leads to a $2 \times 10^{-6} \cdot p$ expanded uncertainty term. Lastly, the best we can do to determine the height of the static pressure head adds another $0.5 \times 10^{-6} \cdot p$ expanded uncertainty. In sum, when comparing the refractometer to the manometer, one would expect agreement within $U(p_{FP})$, $U(p_{UIM})$, plus the additional terms above: for total of $[(9.3 \text{ mPa})^2 + (10.6 \times 10^{-6} \cdot p)^2]^{1/2}$. This uncertainty bound is also plotted in Fig. 2(a). At pressures above 1 kPa there is an obvious $12 \times 10^{-6} \cdot p$ structure to the data. This structure, showing a $\pm 6 \times 10^{-6} \cdot p$ disagreement between the manometer and refractometer at 10 kPa and 40 kPa, is troublesome since it is on the edge of the manometer's stated expanded uncertainty. When we saw this trend one year ago, it was not clear to which instrument to attribute the error. The introduction of a second refractometer to the experiment solves the ambiguity, and gives us a high level of confidence that the error is in the manometer, for the reasons discussed next. [Incidentally, the comparison trend shown Fig. 2(a) reproduces the trend from one year ago to within $2 \times 10^{-6} \cdot p$.]

When comparing two refractometers to one another, many of the systematic uncertainties listed in Tab. I are common to both systems and are not observed. The refractometer-to-refractometer comparison is not prone to the aforementioned acquisition problems since the (frequency) measurement can be synchronously gated; in fact, when both refractometers are at the same pressure, the effective random noise in the measurement of pressure from each instrument is on the order of 0.2 mPa for 10 s to 100 s timescales, which corresponds to 50 fm noise in the measurement of two separate 150 mm optical lengths. (This noise level is similar to what we see when comparing drift in measurement and reference cavity resonances in the same refractometer; the noise level in pressure measurement between two refractometers is more than 100 times lower than noise between two manometers. As a

fraction of total pressure, the noise in a single refractometer measuring 100 kPa is less than 2 parts in 10^9 .) In the refractometer-to-refractometer comparison one would expect agreement

between the two instruments within the combined uncertainty of the terms $\frac{\Delta f}{\nu}$, d_m , and d_r , plus compression hysteresis, anomalous distortion, lock offsets, cavity length drift, thermometer calibration, and the head height correction: for total of $[(1.8 \text{ mPa})^2 + (2.4 \times 10^{-6} \cdot p)^2]^{1/2}$. In Fig. 2(b) we show this uncertainty bound along with the disagreement between pressure measured with the two separate refractometers. As can be seen, there is a systematic error of $6.7 \times 10^{-7} \cdot p$ between the two refractometers; the standard deviation on the disagreement is $8.6 \times 10^{-7} \cdot p$. If a refractometer were a linear device for all compressive pressures, the fact that two instruments agree to within $1 \times 10^{-6} \cdot p$ for $p > 100 \text{ Pa}$ would make a strong case that the $12 \times 10^{-6} \cdot p$ structure in Fig. 2(a) comes from the manometer.

To provide insight into the linearity of each refractometer, we looked at how the reference cavities distorted as a function of pressure. Since the reference cavity is permanently at vacuum, changes in its length can be measured to a few $10^{-12} \cdot L$ by comparing changes in its resonance frequency to an iodine-stabilized laser. For our refractometers $d_r \approx 10^{-11}/\text{Pa}$, and the drift on both reference cavities is about $3.8 \times 10^{-12}/\text{h}$, and thus d_r can not be measured with much confidence below 1 kPa, because the change in resonance of the compressed cavity is small compared to temporal drift in cavity length and iodine-stabilized laser noise; moreover, reliable measurement of distortion at low pressure requires stability in glass temperature on the order of 10 μK . In Fig. 2(c) reference cavity distortion for both refractometers is plotted as a function of pressure. The mean values d_r for each refractometer differ by 0.1 %, and the difference is dependent upon material properties and geometries. The 0.2×10^{-3} deviations from linearity of both reference cavities give us confidence that we know d_r to within $2 \times 10^{-15}/\text{Pa}$. Since our measure of pressure comes from

$\frac{\Delta f}{\nu} \approx 2.65 \times 10^{-9}/\text{Pa}$, as far as compressibility distortions are concerned, we believe the refractometer can hold 10^{-6} reproducibility and linearity throughout the five-decades of pressure in which we are interested.

III. CONCLUSION

We have described comparison measurements of low-pressure between traditional mercury manometry and a novel laser refractometer. The refractometer demonstrates 10^{-6} reproducibility for $p > 100 \text{ Pa}$, and this precision outperforms a manometer. We have developed the expanded uncertainty budget for pressure measurement with a refractometer, $U(p_{\text{FP}}) = [(2.0 \text{ mPa})^2 + (8.8 \times 10^{-6} \cdot p)^2]^{1/2}$. We believe the refractometer is linear to $10^{-6} \cdot p$, and we argue that at pressures below 1 kPa the instrument can transfer the pascal more accurately than a primary realization. For future work we envision a laser refractometer that will measure helium refractivity to a few $10^{-6} \cdot p$: theoretical calculations of helium refractivity¹⁷ will derive a pressure from a measurement of refractivity at a known temperature, thereby allowing us a mercury-free primary realization of the pascal.

Appendix A

Density second virial, B_p

A plot of experimental values for B_p is given in Fig. 3(a), where we have selected values from Dymond *et al*¹⁵ in the range ($290 < T < 310$) K, which have stated uncertainties of 0.3 cm³/mol or less. (The uncertainties stated in Dymond *et al* are represented in Fig. 3(a) by the error bars.) A least-squares fit to the data yields $B_p(T) = -4.571 + 1.974 \times 10^{-1} \cdot (T - 300) - 5.137 \times 10^{-4} \cdot (T - 300)^2$, and the standard deviation on the residuals from the fit is 0.24 cm³/mol. So from the literature surveyed by Dymond *et al*, one would have to conclude $B_p(302.919) = (-4.00 \pm 0.24)$ cm³/mol; if this were the case, uncertainty in B_p would dominate our $U(p_{FP})$ with a $9.7 \times 10^{-6} \cdot p$ contribution for pressures up to 100 kPa.

In Tab. I we state $B_p(302.919) = (-3.973 \pm 0.07)$ cm³/mol. Our value differs from the fit to the Dymond *et al* data, and our expanded uncertainty is lower than any measurement of B_p reported to date. We are confident in our stated value and uncertainty for the following reasons. In Fig. 3(b) we plot disagreement in pressure as measured by the refractometer and manometer. This comparison is the same as Section II-C but with an emphasis on higher pressures, where changes in gas density are larger, and therefore errors in virial coefficients contribute more error to p_{FP} . Importantly, the manometer behaves better above 50 kPa, and the higher pressures also allowed us an independent check on manometer linearity, by comparing it directly (no CDG) against a dead-weight piston gage for pressures 60 kPa, 120 kPa, and 180 kPa: we found disagreement between the two of less than $1 \times 10^{-6} \cdot p$. For the pressure change 60 kPa to 180 kPa, an error in B_p of $\delta B_p = 0.24$ cm³/mol would cause an error in p_{FP} of $11.6 \times 10^{-6} \cdot p$; however, for the same pressure change the quadrature-sum contribution of $\delta B_R = 0.2$ cm⁶/mol² and $\delta C_p = 200$ cm⁶/mol² is only $2.3 \times 10^{-6} \cdot p$. Since error in the refractometer is much more sensitive to B_p than B_R and C_p , we believe the correct value of B_p can be chosen as the one that minimizes the error between the manometer and refractometer, if the manometer and/or piston gage are linear in the range 60 kPa to 180 kPa.

This method of obtaining B_p is similar to that of Häusler and Kerl¹⁸, where density virials were determined by measuring refractivity with an optical interferometer at many pressures on an isotherm, and then choosing the coefficients that minimized deviations of measured refractivity (density) from the Lorentz-Lorenz equation; the difference is that we can determine virial coefficients about 200 times more accurate than that approach, and about 3 times more accurate than state-of-the-art. Indeed, in future work we plan to measure the density virials of nitrogen and argon with the lowest uncertainty reported to date across a larger range of temperatures.

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FIG. 1. Plumbing to compare a laser refractometer to a manometer. Our two laser refractometer systems have separate thermometers and control systems, and have different mirror coatings and distortions. CDG: capacitance diaphragm gage; rp: research purity.

FIG. 2.

(a) Disagreement in pressure as measured by two separate laser refractometers (p_{FP}) and mercury ultrasonic manometer (p_{UIM}); (b) disagreement in pressure as measured by two laser refractometers; (c) distortion linearity of refractometer reference cavities as a function of compressive pressure.

FIG. 3.

(a) A selection of low uncertainty measurements of B_ρ and the fit $B_\rho(T) = -4.571 + 1.974 \times 10^{-1} \cdot (T - 300) - 5.137 \times 10^{-4} \cdot (T - 300)^2$. (b) Disagreement in pressure between the laser refractometer and ultrasonic manometer: if our value of B_ρ were wrong by $\delta B_\rho = 0.24 \text{ cm}^3/\text{mol}$, the measure of pressure in the refractometer would be wrong by almost $12 \times 10^{-6} \cdot p$.

TABLE I

Expanded uncertainty for pressure measured by a laser refractometer. Uncertainties for the parameters from (1) and (2) are estimated for $p = 100$ kPa.

parameter	offset effects	contribution to relative $U(p_{\text{FP}}) \times 10^6$	notes
$A_R = 4.446\,139(30) \text{ cm}^3/\text{mol}$		7.3	<i>i</i>
$B_R = 0.81(20) \text{ cm}^6/\text{mol}^2$		1.8	<i>ii</i>
$C_R = -89(10) \text{ cm}^9/\text{mol}^3$		0.01	<i>ii</i>
$B_p = -3.973(70) \text{ cm}^3/\text{mol}$		2.9	<i>iii</i>
$C_p = 1434(200) \text{ cm}^6/\text{mol}^2$		1.0	<i>iii</i>
$T = 302.919(1) \text{ K}$		3.3	<i>iv</i>
$k_B = 1.380\,648\,5(16) \times 10^{-23} \text{ J K}^{-1}$		1.1	<i>v</i>
$\frac{\Delta f}{\nu} = 2.649422(2) \times 10^{-9} / \text{Pa}$		0.8	<i>vi, vii</i>
$d_r = -1.0918(2) \times 10^{-11} / \text{Pa}$		0.4	<i>vii</i>
$d_m = 9.835(4) \times 10^{-12} / \text{Pa}$		1.3	<i>vii</i>
nitrogen impurity		0.5	<i>viii</i>
compression hysteresis		0.1	<i>ix</i>
outgassing	1.5 mPa		<i>x</i>
anomalous distortion	0.6 mPa		<i>xi</i>
lock offsets	1 mPa		<i>xii</i>
cavity length drift	0.5 mPa		<i>x</i>
expanded uncertainty ($k = 2$)	$[(2.0 \text{ mPa})^2 + (8.8 \times 10^{-6} \cdot p)^2]^{1/2}$		

i Based on the most accurate measurement of nitrogen refractivity¹¹. Knowledge of A_R is limited by how accurate the pascal can be realized.

ii B_R and C_R are based on Ref. 14 and references therein.

iii See Appendix A for a discussion on B_p ; C_p is based on a fit to the data of Dymond *et al*¹⁵ over temperatures close to our range of interest. The value in the table is calculated at 302.919 K from: $C_p(T) = 1432 + 2.923 \cdot (T - 300) - 0.781 \cdot (T - 300)^2$.

iv Measured with a capsule SPRT and includes $U(T - T_{90})$ ¹⁶.

v From most recent CODATA¹³.

vi Includes errors in the estimate of cavity length, mirror and diffraction phase shifts, and vacuum-wavelength.

vii These terms are specific to one of our FP cavities. In principle, the terms are correlated with uncertainty already expressed in A_R , and their contribution to $U(p_{\text{FP}})$ is smaller than what is stated.

viii Worst-case is 0.0001 % CO₂ in 99.9999 % N₂.

ix Our FP cavity is made of monolithic ULE, which has notably low hysteresis.

x For measurements completed 0.5 h after a fill.

^{*xi*}For temperature changes of 0.5 mK or less. This distortion is caused by a few $10^{-9}/\text{K}$ nonuniformity in the thermal expansion coefficient of ULE.

^{*xii*}Caused by residual amplitude modulation and offsets in electronics.