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Pascal Realization by Comb-Spectral-Interferometry Based Refractometer *

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To break through the limitations of existing pressure standards, which rely on the gravity and toxic mercury, the national metrological institutes prefer a quantum-based pressure standard. Combining the ideal gas law with helium refractivity measurement, we demonstrate a scheme for the realization of the pressure unit. The refractometer is based on a spectral interferometry with an optical frequency comb and a double-spaced vacuum cell. Through fast Fourier transform of the spectral interferograms of the two beams propagating inside and outside the vacuum cell, the helium refractivity can be obtained with a combined standard uncertainty $u(n)$ of 2.9×10^{-9}. Moreover, the final $u(p)$ is $\sim 8.7 \times 10^{-6}$ in a measurement range of several megapascals (MPa). Our apparatus is compact, fast (15 ms for one single measurement) and easy to handle. Furthermore, the measurement uncertainty will be improved to $\sim 1 \times 10^{-9}$ or lower if a VIPA-based spectrometer is used. The value of $u(p)$ will thus increase to 3×10^{-6} or better in several MPa.

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Since pressure is a basic parameter of thermodynamics, high-accuracy measurement of pressure is of great significance in both fundamental research on thermodynamic properties of gas and industrial applications. For centuries, the unit of pressure has been defined by the relation of force per unit area. At present, the most commonly used standards for gas pressure are liquid-column U-tube manometers suitable for lower pressure (up to 100 kPa) and piston gauges suitable for higher pressure (up to 1000 MPa), which all depends on the gravity.[1] For example, the mercury-based manometer in the National Institute of Standards and Technology (NIST) is the most accurate pressure standard over all the world.[2] However, the current drawbacks including slowness, huge size, toxic mercury, and high cost limit its applications. Moreover, it is not easy to operate and maintain. Recently, the trend of metrology in the world is to define the basic quantities on the numerical values of the basic physical constants.[3] In the context of the modifications planned for the international system of unit (SI) in 2018, the Boltzmann constant will be set as a fixed value,[4,5] which makes the thermodynamic definition (relying on the ideal gas law) a more promising method to establish a new generation of pressure standard.

In 1998, Moldover in NIST first demonstrated the possibility of realizing the thermodynamic pressure standard based on an ideal gas equation of state and polarizability virial equation,[6] from which the relationship between pressure and gas polarizability can be built. The key problem to be solved for this scheme is the precise measurement of gas polarizability and gas virial coefficients. According to the development of *ab initio* quantum calculations, since the theoretical calculation precision of the helium (He) density virial coefficients has exceeded the best experimental results and the computing level is still rising,[7–12] the relation of refractivity to pressure with a high accuracy is only possible for He at present, due to the complexity of other atoms or molecules. Puchalski *et al.* calculated the He polarizability with an uncertainty of 1×10^{-7},[13] which is at the highest level up to now. The quantum calculations thus provide a theoretical basis for defining the pressure standard with helium refractivity.

To measure the dielectric permittivity of He ($\varepsilon_{\rm r}$) or He refractivity (n,$n = \sqrt{\varepsilon_{\rm r}\mu_{\rm r}}$), Moldover put forward the capacitance comparison method to measure $\varepsilon_{\rm r}$ and the theoretical measurement uncertainty is 2×10^{-9}.[6] For this reason, Buckley *et al.* designed a toroidal cross capacitor,[14] but the measurement uncertainty of $\varepsilon_{\rm r}$ is only 3.8×10^{-7} limited by the electric bridge. Because the measurement accuracy of the commercial electric bridge is only on the order of 10^{-6}, there is great difficulty in realizing the thermodynamic pressure standard based on the capacitance method. To improve the measurement uncertainty of $\varepsilon_{\rm r}$, May *et al.* made a quasi-spherical microwave cavity resonator to obtain $\varepsilon_{\rm r}$ from the change of resonance frequency and the measurement uncertainty reaches 1.7×10^{-7}.[15] Considering the amendments of $\mu_{\rm r}$ and the dispersion of $\varepsilon_{\rm r}$, Schmidt *et al.* measured the molar polarizability of He with a measurement uncertainty of 9.1×10^{-6} using the same method,[16] amounting to $6.3 \times 10^{-9} \times p/\text{MPa}$ of the measurement uncertainty of $\varepsilon_{\rm r}$.

Restricted by the measurement principles, the capacitance comparison method and the microwave cavity resonator method are close to their measurement

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limits. Consequently, to make a breakthrough, a new measurement principle should be adopted. As is known, the relationship between n and the molar density for an isotropic homogeneous medium is derived from the Lorentz–Lorenz equation.[17] Since optical methods can measure the molar density accurately in the process of light-matter interaction, optical methods are attractive alternatives to measure the refractive index. NIST has designed a Fabry–Perot cavity made of ultra low expansion glass and measured the refractive index with high precision by measuring its resonant frequencies when the cavity is at vacuum and filled with gas.[18–20] However, it is time-consuming and the fluctuations in gas pressure cannot be avoided during the measurement. To eliminate the pressure distortions, Stone *et al.* obtained the refractive index by measuring the same physical displacement of a cavity of variable length in a vacuum and in gas at constant pressure.[21] Nevertheless, it is a very large challenge to maintain the changes in physical lengths of different cavities so they are always the same. Moreover, below spring forces fluctuate with displacement and might deform the relative positions of the cavity mirrors. More recently, Egan *et al.* measured the optical refractivity of He via integration of a triple-cell into a quasi-monolithic heterodyne interferometer.[22] Nonetheless, the interferometer should be placed in a system where environmental parameters are kept in strict control. To solve the above shortcomings, in this Letter, we present an absolute refractometer to measure the refractivity of He with high accuracy in real time for pascal realization.

Resulting from the extinction theorem, the Lorentz–Lorenz equation for helium is expressed as[17]

$$L_n = \frac{n^2-1}{n^2+2}, \tag{1}$$

where L_n is just a symbol representing Eq. (1), and n is the He refractivity.

The virial equation of state for real helium gas can be illustrated by the power series of ρ,

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3 + \cdots), \tag{2}$$

where p and T are the thermodynamic pressure and temperature, respectively, ρ is the molar density of He, R is the molar gas constant ($R = k_{\rm B}N_{\rm A}$), and B, C, and D are the He density virial coefficients of the second order, third order, and fourth order, which are determined on T.

Considering the interatomic forces of He, L_n can be written in a similar way to Eq. (2),

$$L_n = A_{\rm r}\rho\Big(1 + \frac{B_{\rm r}}{A_{\rm r}}\rho + \frac{C_{\rm r}}{A_{\rm r}}\rho^2 + \frac{D_{\rm r}}{A_{\rm r}}\rho^3 + \cdots\Big), \tag{3}$$

where $A_{\rm r}$, $B_{\rm r}$, $C_{\rm r}$, and $D_{\rm r}$ are the He refractivity virial coefficients of first, second, third, and fourth orders, respectively, which are dependent on polarizability, and the diamagnetic susceptibility of He. Moreover, these coefficients are also related to the thermodynamic temperature.

According to the Lorentz–Lorenz equation (Eqs. (1) and (3)) and the virial equation of state (Eq. (2)), the thermodynamic pressure p can be expanded in the power series of L_n as follows:

$$p = \frac{RT}{A_{\rm r}}L_n\Big[1 + \frac{A_{\rm r}B - B_{\rm r}}{A_{\rm r}^2}L_n + \frac{A_{\rm r}(A_{\rm r}C - C_{\rm r}) - 2B_{\rm r}(A_{\rm r}B - B_{\rm r})}{A_{\rm r}^4}L_n^2 + \cdots\Big], \tag{4}$$

where the density virial coefficients and refractivity virial coefficients can be theoretically calculated from *ab initio* calculation and the first principle with sufficient accuracy.[13,23] Moreover, because $k_{\rm B}$ and $N_{\rm A}$ will be defined as constants with no contributed uncertainty in the new SI,[24] R will also have an exact value. Therefore, only by measuring the refractive index of helium in real time, can the thermodynamic pressure of helium then be obtained. In addition, if p is known from other methods, the refractive index measurement can be used to realize the kelvin consistent with the *Mise en Pratique*.[25,26] Furthermore, if p and T are given by other means, $k_{\rm B}$ can be acquired from the refractive index of He.

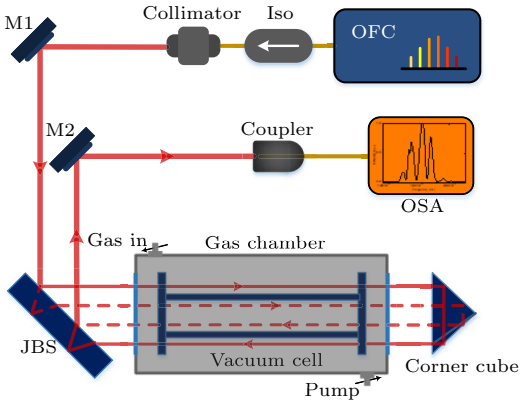

Fig. 1. Experimental apparatus of the gas refractometer. Iso: isolator; M1, M2: mirror. The red line denotes the light beam propagating in the free space (the dotted line represents the light beam transmitting inside the vacuum cell), the yellow line illustrates the light beam passing through the single mode optical fiber.

The experimental apparatus of our refractometer is shown in Fig. 1. One 250-MHz optical frequency comb (OFC, Menlo Systems GmbH, FC1500) with the central wavelength and 3-dB bandwidth of 1563 nm and 50.3 nm is utilized as the light source. This refractometer employed the Jamin interferometric measurement system based on a double-spaced vacuum cell whose inner space is evocated to a vacuum and outer space is connected with the atmosphere. The vacuum cell is made of fused silica and positioned in one gas chamber with two fused-silica windows. The gas to be measured can be filled in or pumped out via two pipes linked to the chamber. The output from the

light source will be divided into two beams with nearly equal light intensity through a Jamin beam splitter (JBS). Next, these two light beams will separately propagate in the internal and external part of the vacuum cube, and then, they will interfere with each other on the upper surface of the JBS. From one single interference, the interferometric intensity at multi-wavelengths can be obtained at the same time. Finally, a commercial optical spectrum analyzer (OSA, Agilent, 86140B) is applied to record the dispersive interference spectrum.

The dispersive interference information is expressed by the spectral power density $S(f)$, which is a function of the optical frequency f as follows:

$$S(f) = S_0(f) + S_m(f)\cos\varphi(f), \tag{5}$$

where $S_0(f)$ is the mean intensity of the two beams, $S_m(f)$ is the modulation amplitude, and $\varphi(f)$ is the interferometric phase difference expressed as $\varphi(f) = 2\pi f\alpha$ (α is the optical path delay computed as $2(n-1)L/c$, L is the geometric length of the double-spaced cell, and c is the speed of light in a vacuum). Considering the expression of $\varphi(f)$, the complex form of $S(f)$ is expressed as

$$\begin{aligned} S(f) = S_0(f) + \frac{1}{2}[&S_m(f)\exp(i2\pi f\alpha) \\ &+ S_m(f)\exp(-i2\pi f\alpha)], \end{aligned} \tag{6}$$

where $i = (-1)^{1/2}$. Then Eq. (6) is Fourier-transformed and the result is as follows:

$$\begin{aligned} X(t) &= FT\{S(f)\} \\ &= X_0(t) + X_m(t) \otimes \pi[\delta(t+\alpha) + \delta(t-\alpha)], \end{aligned} \tag{7}$$

where $\delta(t)$ is a Dirac delta function, while $X_0(t)$ and $X_m(t)$ are the Fourier transforms of $S_0(f)$ and $S_m(f)$, respectively. To determine the exact value of α, the peak at $t = \alpha$ is isolated by a band-pass filter and then inverse Fourier-transformed, whose result is derived as

$$\begin{aligned} S'(f) &= FT^{-1}\{X_m(t) \otimes \pi\delta(t-\alpha)\} \\ &= \pi S_m(f)\exp(\mathrm{j}\varphi(f)). \end{aligned} \tag{8}$$

Subsequently, $\varphi(f)$ can be obtained through the arctangent operation and the gas refractive index is calculated from the expression[27]

$$(n-1) = \left(\frac{c}{4\pi L}\right)\frac{d\varphi(f)}{df}. \tag{9}$$

To confirm the feasibility and performance of the gas refractometer, ambient air was measured using our refractometer due to simplicity, convenience, and lower cost. This successive measurement lasted ~10 h and the experimental parameters are monitored via corresponding sensors to provide comparative data by Ciddor's equation.[28] Figure 2 shows the changes of environmental parameters and Fig. 3 illustrates the measured results of air refractive index. We can find in Fig. 3(a) that the variation trends of the measured data and computed results from Ciddor's equation are almost identical. In addition, we can see from Fig. 3(b) that their differences are less than 6.6×10^{-9} with a standard deviation of 4.2×10^{-9}, which demonstrates that our apparatus performs a good stability. The refractive index of He can also be measured by filling pure helium into the gas chamber.

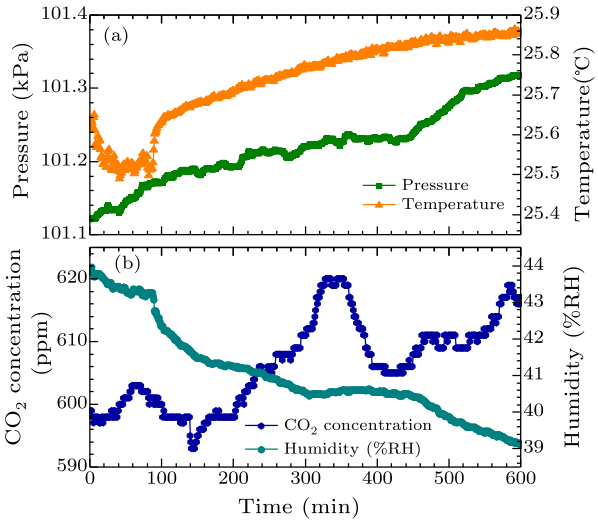

Fig. 2. The 10-h measurements of the environmental parameters. (a) Pressure and temperature data in the experiment. (b) Humidity and CO_2 concentration data in the experiment.

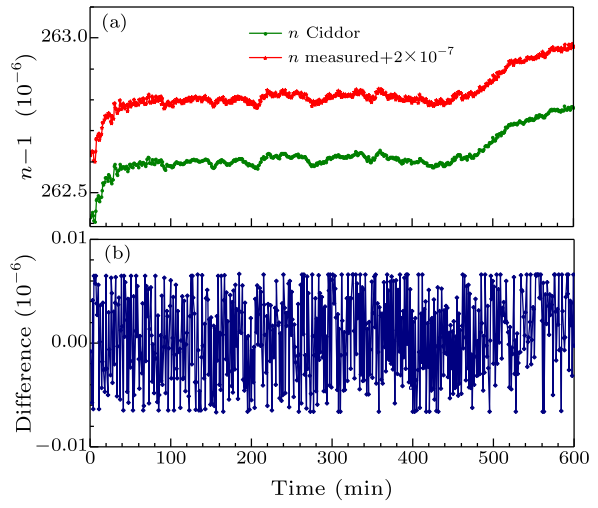

Fig. 3. The 10-h measurement of the air refractive index. (a) Comparison between the measured data and computed value from Ciddor's equation, noticing that to separate the two curves, the measured data is added by 2×10^{-7} for better visualization. (b) Difference between the two methods.

The measurement system mainly includes four error sources. As for the frequency error, it incorporates the sampling frequency nonlinearity of the OSA and the frequency stability of the optical comb. In our experiment, the nonlinearity error contributes

1×10^{-5} and the frequency stability is 2.4×10^{-11} (1 s). Thus the frequency error contributes 1×10^{-5} to the measurement uncertainty of $(n-1)$. For the computing error of interferometric phase difference by FFT, we have simulated the calculation process on the computer and found that the calculation accuracy of the phase difference is $\sim 1 \times 10^{-9}$. As for the length error of the vacuum cell, first of all, the length of the vacuum cell is measured by a coordinate measuring machine (Hexagon Metrology, Optiv Performance 543) as 396.000 mm with an accuracy of about 0.5 μm. Secondly, the path difference caused by the non-parallelism between the cell and the optical axis is about 0.2 μm. Thirdly, the temperature change caused error is 0.6 μm. Lastly, the window deformation introduced by atmospheric pressure difference is 0.56 μm. Therefore, the entire length error contributes $\sim 4.7 \times 10^{-6}$ to the relative measurement uncertainty of $(n-1)$. As for the vacuum degree inside the vacuum cell, because the ambient air inside was first evacuated below 0.01 Pa using a turbomolecular vacuum pump, the relative uncertainty of $(n-1)$ caused by residual gas would not be larger than 1×10^{-7} according to Ciddor's equation. Those four error sources bring a combined standard uncertainty of 1.1×10^{-5} to $(n-1)$ following the guide to the expression of uncertainty in measurement. Seen from Eq. (9), the measured object is $(n-1)$ but not n, which brings remarkable benefits.[29] From the mathematical derivation of $dn/n = (n-1)/n \cdot d(n-1)/(n-1)$, we find that the relative uncertainty of n improves $1/(n-1)$ times under the same conditions. Consequently, the combined standard uncertainty of the gas refractometer is $(n-1) \times 1.1 \times 10^{-5}$. Under general circumstances, the air refractivity is nearly equal to 1.00027 and $(n-1)$ is $\sim 2.7 \times 10^{-4}$, then the combined standard uncertainty of air is 3×10^{-9}. As for helium, the combined standard uncertainty is $\sim 2.9 \times 10^{-9}$. According to the Lorentz–Lorenz equation and the virial equation of state, the contribution of $u(n)$ to the measurement uncertainty of pressure $(u(p))$ is $3 \times 10^3 u(n)/(p/\mathrm{MPa})$, thus the final $u(p)$ is $\sim 8.7 \times 10^{-6}$ in a measurement range of several MPa.

In conclusion, we have demonstrated a real-time absolute gas refractometer capable of measuring the helium refractivity with a combined standard uncertainty of 2.9×10^{-9} at 1563 nm for the realization of the pressure standard using spectral interferometry of the frequency comb. The final measurement uncertainty of pressure achieves 8.7×10^{-6} in a measurement range of several MPa. If a VIPA-based two-dimensional spectrometer is used to record the dispersive spectrum, the measurement uncertainty of the refractive index will be improved to $\sim 1 \times 10^{-9}$ or lower and $u(p)$ will thus increase to 3×10^{-6} or better in several MPa. Our apparatus is simple, compact, and easy to handle, which has great potential to develop portable pressure standards in the future. Moreover, one single measurement only takes 15 ms, which has obvious advantages over the traditional mercury pressure gauge. In practical applications, precise measurement of atmospheric pressure can improve the measurement accuracy of aircraft height. Moreover, this kind of pressure standard does not depend on the gravity field, so that it can also be applied to the traceability of the pressure metrology in a microgravity environment such as space station.

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