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Polarizability of molecular hydrogen and gas metrology

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The polarizability of the hydrogen molecule can be precisely calculated based on the quantum electrodynamics (QED) theory and a few fundamental physical constants. Therefore, experimental measurements with comparable accuracy can test the theory and establish gas metrology with hydrogen as the working gas. An optical refractometer was built and its performance was tested by measuring the electric dipole polarizabilities of argon, neon, and nitrogen. The polarizability of the H_2 molecule was determined to be 2.031 027(71) $\mathrm{cm}^3\,\mathrm{mol}^{-1}$. The result agrees with the current calculated value, indicating the potential of a primary standard for pressure or temperature through measuring the polarizability of H_2.

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I. INTRODUCTION

As the simplest and most abundant neutral molecule in the universe, the hydrogen molecule has long been a testing ground for quantum mechanics theory and high-level quantum chemistry calculations. The accuracy of the transition frequencies of the hydrogen molecule has been improved continuously in the last century and recent measurements reached the 10^{-9} accuracy [1–6]. Theoretical calculations also achieved an accuracy of 10^{-8} by including the relativistic [7] and quantum electrodynamics (QED) corrections [8,9] up to the order of α^4 based on the Born-Oppenheimer approximation, where α is the fine structure constant. Nonadiabatic QED corrections to the order of α^3 have also been numerically calculated [10]. However, the comparison between experimental and theoretical studies has been limited to the transition frequencies of different isotopologs of molecular hydrogen.

Electric polarizability is another important property of an atom or molecule, which decides the response to an external electric field. Refractive-index gas metrology (RIGM) [11–13] using a working gas with "calculable" polarizability is attractive for a primary standard realizing the SI units of degrees Kelvin or Pa [14–16]. The polarizability of helium has been calculated to an accuracy of 0.1 parts per million (ppm) [17] by taking into account the QED corrections at the order of α^3. However, the permeation of helium in ultra-low-expansion (ULE) materials [18,19] presents an obstacle to an optical refractometer with helium as the working gas. Pressure measurement with an extended uncertainty of 8.8 ppm ($k = 2$) has been demonstrated by a nitrogen-based gas refractometer device [20]. However, the accuracy of the calculated polarizabilities of nitrogen [21], argon [22], and neon [23] can hardly exceed the level of 10^{-4}, which prevents a primary standard based on these gases.

Here, we present the measurement of the polarizability of the hydrogen molecule using an optical refractometer. The polarizability of the hydrogen molecule was measured with very limited precision [24,25]. Sun *et al.* recently calculated [26] the static electric dipole polarizabilities of low-lying rotational levels of the hydrogen molecule without using the Born-Oppenheimer approximation. Calculation of the α^4 QED corrections for the hydrogen molecule is also feasible [9,17,27]. The precise determination of the polarizability of the hydrogen molecule allows us to explore the possibility of realizing a primary refractive-index gas thermometry (RIGT) using H_2, and a comparison with high-level *ab initio* calculations also provides another scheme for testing the QED theory.

II. EXPERIMENT

The method of the optical measurement of polarizability is to use a resonant cavity to measure the refractive index n of the working gas, which is related to the pressure p and temperature T of the gas [16,28],

$$\frac{p}{RT} = \frac{2(n-1)}{3(A_\varepsilon + A_\mu)} + (n-1)^2 \times \left[\frac{4B_T}{9(A_\varepsilon + A_\mu)^2} - \frac{A_\varepsilon^2 + 4B_\varepsilon + 6A_\varepsilon A_\mu}{9(A_\varepsilon + A_\mu)^3}\right] + O(n-1)^3, \tag{1}$$

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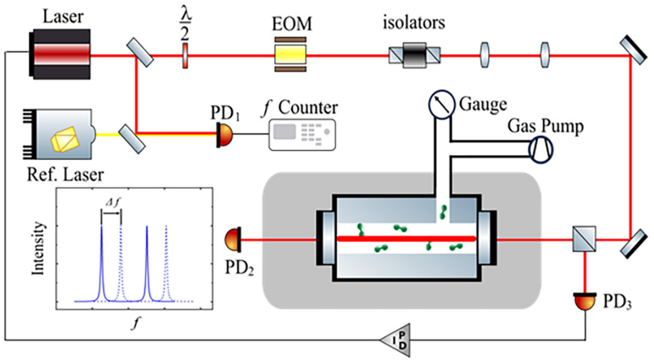

FIG. 1. Schematic diagram of the experimental setup. The mode frequency of an optical cavity made of ULE is measured from the beating signal between a laser locked to the cavity and a frequency-stabilized reference laser. When the ULE cavity is filled with working gas, the frequency change is measured to determine the refractive index of the gas.

where $R = 8.314\,462\,6$ J mol^{-1} K^{-1} is the molar gas constant, A_ε is the molar electric polarizability, A_μ is the molar magnetic polarizability, B_T is the second virial coefficient, and B_ε is the second dielectric virial coefficient.

Figure 1 shows the schematic configuration of the experimental setup. The laser source is a 1566-nm fiber laser with a linewidth of less than 10 kHz. The laser is locked to a longitudinal mode of a Fabry-Pérot type optical cavity by a Pound-Drever-Hall (PDH) locking servo. The optical cavity consists of a 10-cm-long ULE spacer and two highly reflective ($R \approx 99.9\%$) mirrors. The free spectral range is about 1.5 GHz and the cavity mode linewidth is about 0.4 MHz. The optical cavity is placed in a stainless steel vacuum cell, and the cell is placed in a cylinder made of aluminum alloy. The aluminum cylinder is heated to about 297.53 K and the temperature is controlled by a feedback servo. The temperature of the optical cavity is measured by a calibrated platinum resistance thermometer. A homemade frequency-stabilized laser is used as a frequency reference, and its frequency drift has been measured to be about 0.1 Hz/s. The beat frequency between the probe laser and the reference laser is recorded to determine the cavity mode frequency.

During the experiment, we measured the frequencies of the cavity mode before and after filling the working gas. The frequency change $\Delta\nu$ is related to the refractive index n [13],

$$n - 1 = \frac{\Delta\nu}{\nu_f} + \Delta p\left(\frac{1}{3K} + d\right), \tag{2}$$

where ν_f is the mode frequency of the cavity filled with gas; K is the bulk modulus of the cavity material, $K \approx 3.3 \times 10^{10}$ Pa for ultra-low-expansion (ULE) glass; and d (in Pa^{-1}) is the correction factor for the pressure deformation of the cavity mirrors [29]. Under moderate pressures ($p \lesssim 1$ bar), the contribution of the Δp term is relatively small and can be substituted with an approximate value.

We measured the polarizability with a laser of 1566 nm, and the dipole oscillator strength distribution (DOSD) theory [30,31] was applied to convert the wavelength-dependent dynamic polarizability $A'_\varepsilon(\omega)$ to static electric dipole polarizability A_ε,

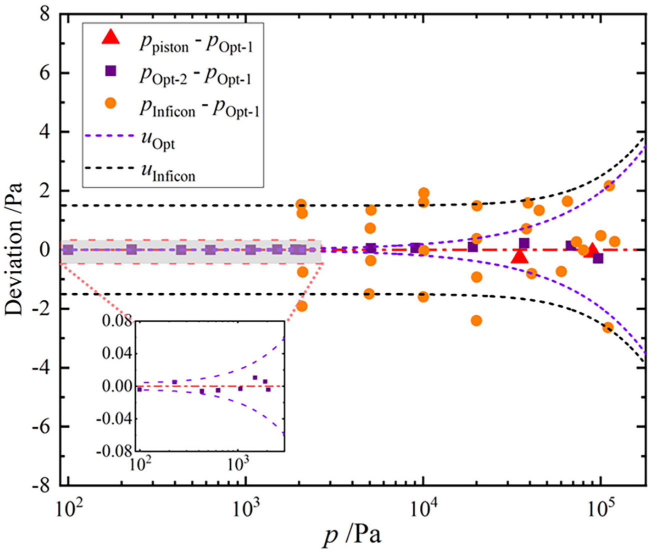

FIG. 2. Comparison of the pressure gauges, the piston, the optical Opt-1 and Opt-2, and the Inficon manometer.

$$A'_\varepsilon(\omega) = A_\varepsilon + \frac{4}{3}\pi N_A a_0^3\left(1 + \frac{m_e}{m_N}\right)^3 \times \left[S(-4)\omega^2 + S(-6)\omega^4 + S(-8)\omega^6\right], \tag{3}$$

where $S(-4)$, $S(-6)$, and $S(-8)$ are the expression dipole sums, a_0 is the Bohr radius, m_e and m_N are the electron and nuclear masses, $\omega = 45.563\,978\,23/\lambda$ is the laser frequency in atomic units, and λ is the vacuum wavelength in nanometers. Parameters for gases of argon, neon, nitrogen, and hydrogen are summarized in Table I.

We installed two optical refractometers [38], hereinafter referred to as "Opt-1" and "Opt-2," respectively. Both systems use ULE cavity cylinders, therefore we assume they have the same bulk modulus $K_1 = K_2$. However, the cavity mirrors are different: Opt-1 uses two fused silica mirrors, Opt-2 uses two ULE mirrors, and we have the pressure deformation correction factors $d_1 \neq 0$ and $d_2 = 0$. A piston pressure gauge (Fluke, PG7601) has been applied to calibrate both refractometers with argon as the working gas. The piston has a stated uncertainty of 11 ppm ($k = 1$) and can be traced back to the pressure reference of the National Institute of Metrology (NIM). The results are shown as two red triangles in Fig. 2. The results at 70 kPa were used to calibrate the optical gauges. Taking $A_\varepsilon = 4.140\,686(10)$ cm^3 mol^{-1} [39], we determined the parameters for Opt-1 and Opt-2 according to Eqs. (1)–(3): $K_1 = K_2 = 3.3372 \times 10^{10}$ Pa, $d_1 = 1.6119 \times 10^{-13}$ Pa^{-1}, and $d_2 = 0$. The other triangle point at 39 kPa shows a deviation between the piston and Opt-1 of -0.3 Pa (-8 ppm), which is within the uncertainty of the piston. The long-term stability was tested by measuring the differences between Opt-1 and Opt-2 many times using argon gas in the range of 90 Pa to 100 kPa, and the results are shown as purple squares in Fig. 2. The purple dashed lines indicate the uncertainty of the optical gauge, $u_{\mathrm{OPT}} = \sqrt{(20 \times 10^{-6} p)^2 + (4\ \mathrm{mPa})^2}$. We can see all the experimental

TABLE I. Parameters used in the determination of the polarizabilities of Ar, Ne, N_2, and H_2. Values of A_μ are from Refs. [32,33], B_T from Ref. [34], B_ε from Refs. [35–37], and S parameters are from Ref. [21].

	Ar	Ne	N_2	H_2
$A_\mu \times 10^6$ ($\mathrm{cm^3\,mol^{-1}}$)	−80.9(6)	−29.2(6)	−52.1(4)	−17.0(5)
B_T ($\mathrm{cm^3\,mol^{-1}}$)	−16.1(5)	11.0(5)	−5.5(3)	14.1(1)
B_ε ($\mathrm{cm^6\,mol^{-2}}$)	1.72(11)	−0.0930(5)	1.12(30)	0.06(10)
$S(-4)$ (a.u.)	27.91(7)	2.886(2)	30.11(9)	19.96(8)
$S(-6)$ (a.u.)	95.06(50)	5.063(18)	101.8(9)	82.94(51)
$S(-8)$ (a.u.)	391(9)	10.86(4)	385(6)	367(4)

deviations are within this uncertainty curve, indicating a very stable performance of both optical gauges during the experiment lasting over 1 yr.

A capacitance manometer (Inficon Cube CDGSci, 1000 Torr) was used to measure the gas pressure. The manufacturer-stated accuracy of the manometer is 0.025%, and the repeatability is better than 0.005%. It was further calibrated by the optical refractometer. The orange dots in Fig. 2 show the deviations of Inficon manometer readings from the optical gauge Opt-1, and the black dashed line shows the uncertainty of the calibrated Inficon manometer $u = \sqrt{(20 \times 10^{-6} p)^2 + (1.5\ \mathrm{Pa})^2}$.

III. RESULTS AND DISCUSSION

A. Uncertainty budget

Table II shows the uncertainty budget in the polarizability measurement in this paper. The cavity temperature was measured by a NIM-calibrated platinum resistance thermometer, and the uncertainty is below 5 mK, corresponding to a fractional uncertainty of 16 ppm in the polarizability. The uncertainty of the Inficon manometer has been given by the conclusion of Sec. II B, which is 25 ppm at 1 bar. The bulk modulus of the optical cavity has been determined by a piston gauge with an accuracy of 11 ppm. Therefore, the same uncertainty was assigned to the value of K.

TABLE II. The uncertainty budget (in 10^{-6}, ppm) of the static polarizability of N_2, Ne, and H_2 gases.

	N_2	Ne	H_2
T	16	16	16
p	25	25	25
K	11	11	11
Gas purity	1	1	1
Outgas	0.2	0.9	0.5
Frequency	<0.1	<0.1	<0.1
L_{cav}	<0.1	<0.1	<0.1
Statistics	9	26	5
A_μ	0.1	0.6	0.2
B_ε	3	<0.1	2
B_T	12	20	4
$S(i)$	7	1	12
Total	36	46	35
		A_ε ($\mathrm{cm^3\,mol^{-1}}$)	
This work	4.38705(16)	0.994742(46)	2.031027(71)
Expt.[a]	4.38679(7)	0.9947114(24)	2.033(4)
Theor.[b]	4.3887(18)	0.99470(13)	2.03080(12)

[a] Experimental values of N_2, Ne, and H_2 are from Refs. [40], [39], and [25], respectively.

[b] Theoretical values of N_2, Ne, and H_2 are from Refs. [21], [23], and [26], respectively.

In all the measurements, sample gases with 99.9999% purity were used and an uncertainty of 1 ppm was given to the uncertainty due to contaminations in the sample gases. Outgas from the vacuum chamber could also affect the measurement. We tested the effect by measuring the frequency drift with the chamber separated from the vacuum line. The drift was at the level of 1 Hz/s. We also noticed a fluctuation of about 2 kHz in the beating frequency recorded in the measurement, which could be a result of the temperature-dependent drift of the locking reference in the PDH locking servo. Note that the frequency change ($\Delta\nu$) is about 48, 12, and 23 GHz from N_2, Ne, and H_2, and the deviations due to outgassing are all below 1 ppm for a measurement typically lasting 3 h. The thermal expansion coefficient of the optical cavity at the experimental temperature is 3×10^{-9}/K. Taking a temperature uncertainty of 5 mK, the thermal expansion of the optical cavity also contributes to a deviation in the determined polarizability, but the influence is below 0.1 ppm in this paper.

The values of the second dielectric virial coefficient B_ϵ and the second virial coefficient B_T are temperature dependent and the uncertainties increase with pressures. Their values and references have been given in the previous section. The uncertainties in the expression dipole sums $S(i)$ ($i = -4, -6, -8$) given in Table I also contribute to the uncertainty budget when converting the measured dynamic polarizability measured at 1566 nm to the static polarizability [21]. They were evaluated according to Eq. (3), as 7, 1, and 12 ppm for nitrogen, neon, and hydrogen, respectively.

B. N_2

Figure 3(a) shows the molar polarizabilities of N_2 determined by Opt-1 at different pressures in the range of 2–100 kPa. Polarizability at a wavelength of 1566 nm was derived according to Eqs. (1) and (2) at each pressure. Due to the large fractional uncertainty from the pressure measurement at low pressures, uncertainties in these data are also larger than others. The dashed line and the purple belt show the weighted average value and the uncertainty at 1566 nm. The static electric dipole polarizability was determined according to Eq. (3), which is $A_\varepsilon^{N_2} = 4.387\,05(16)\ \mathrm{cm^3\,mol^{-1}}$

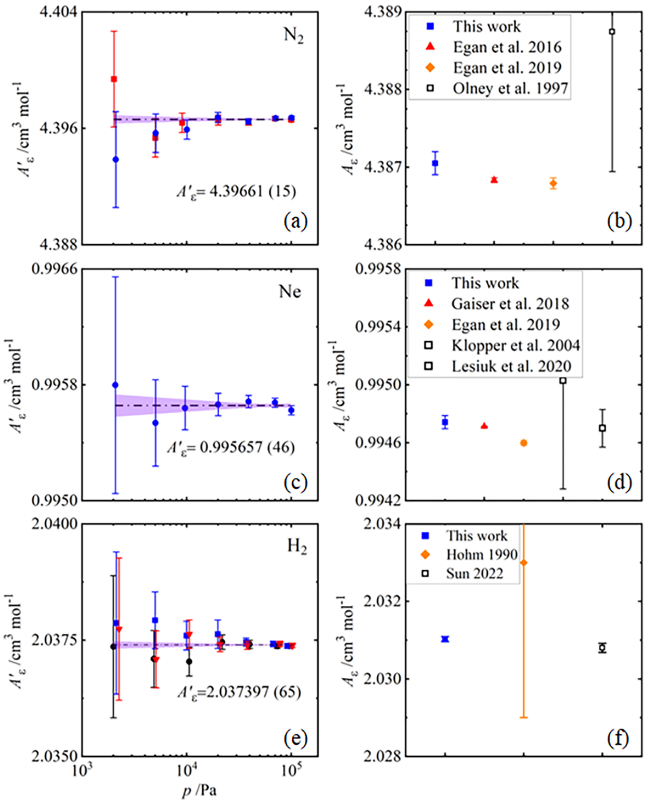

FIG. 3. Polarizabilities of N_2, Ne, and H_2. (a) Polarizability of N_2 at 1566 nm under different pressures measured in this work. Two series of measurements performed in November 2022 and June 2023 were shown with red squares and blue circles, respectively. (b) Static polarizability of N_2 compared with literature values. (c) Polarizability of Ne at 1566 nm under different pressures measured in this work. (d) Static polarizability of Ne compared with literature values. (e) Polarizability of H_2 at 1566 nm under different pressures measured in this work. Results measured on June 2023, December 2023, and January 2024 are shown with black circles, blue squares, and red triangles. (f) Static polarizability of H_2 compared with literature values. Shadows in (a), (c), and (e) show the 1σ confidence region of the averaged value.

with an uncertainty of 36 ppm. A comparison between this work and the literature values is given in Table II and shown in Fig. 3(b). The static polarizability according to the value obtained by Egan *et al.* [40] is 4.386 79(7) $\text{cm}^3\,\text{mol}^{-1}$, agreeing with our value. The theoretical value given by Olney *et al.* [21] is 4.3887(18) $\text{cm}^3\,\text{mol}^{-1}$ with an uncertainty of 410 ppm.

C. Ne

Figure 3(c) shows the molar polarizabilities of neon measured by Opt-1 at different pressures in the range of 2–100 kPa. The weighted average value corresponds to a static electric dipole polarizability of $A_\varepsilon^{\text{Ne}} = 0.994\,742(46)\,\text{cm}^3\,\text{mol}^{-1}$. The value agrees well with the most precise experimental result of 0.994 711 4(24) $\text{cm}^3\,\text{mol}^{-1}$ reported by Gaiser *et al.* [39]. Egan *et al.* [40] gave a value of 0.994 598(16) $\text{cm}^3\,\text{mol}^{-1}$, with a 7σ deviation from the value by Gaiser *et al.* and a 3σ deviation from this work. The theoretical values are with much lower accuracy, as 0.995 03(75) $\text{cm}^3\,\text{mol}^{-1}$ by Klopper *et al.* [41] and 0.994 70(13) $\text{cm}^3\,\text{mol}^{-1}$ by Lesiuk *et al.* [23].

D. H_2

The same method was applied to measure the molar polarizability of H_2. Hydrogen gas samples with a stated purity of 99.9999% were from Air Liquide and a cold trap cooled with liquid nitrogen was applied to remove contaminants in the sample before use. Figure 3(e) shows the polarizabilities of H_2 measured by Opt-1 at different pressures in the range of 2–100 kPa. We carried out three series of measurements and the results are shown in different colors. The weighted average value yields an electric dipole polarizability of molecular hydrogen:

$$A_\varepsilon^{H_2} = 2.031\,027(71)\,\text{cm}^3\,\text{mol}^{-1}\ (297.53\ \text{K}). \tag{4}$$

Our value agrees with the previous experimental value of 2.033(4) $\text{cm}^3\,\text{mol}^{-1}$ given by Hohm and Kerl [25], and the accuracy has been improved by a factor of 50. Sun *et al.* [26] calculated the static polarizability of H_2 at different rotational levels using variationally generated wave functions in Hylleraas coordinates, which yields a polarizability of 2.030 80(12) $\text{cm}^3\,\text{mol}^{-1}$ at 297.53 K. Note that the contributions from the relativistic and QED effects have not been included in the calculation. According to the calculation of atomic helium by Puchalski *et al.* [17], the relativistic term contributes 58 ppm to the total polarizability, and the contribution from QED terms amounts to 22 ppm. Schwerdtfeger and Nagle [42] concluded that the contribution is 55 ppm due to the relativistic effects in the polarizability of atomic hydrogen. Therefore, an estimate of 60 ppm was given for the calculated molar polarizability of H_2 [26]. The polarizability of H_2 obtained in this work agrees with the theoretical value with a deviation of $0.000\,23(7)_{\text{expt}}(12)_{\text{theor}}\ \text{cm}^3\,\text{mol}^{-1}$.

Deuterated hydrogen molecules, HD and D_2, also present in molecular hydrogen samples. According to the calculation by Sun *et al.* [26], the polarizabilities of HD and D_2 are 0.6% and 1.3% lower than that of H_2, respectively. Given the natural D/H isotopic ratio of about 0.0156%, the polarizability of natural hydrogen gas should be corrected by -2×10^{-6} relative to the value of pure H_2. Experimental determination of the polarizabilities of HD and D_2 could help validate the method and underlying theory. However, the accuracy of such measurements is currently limited by the challenges in determining the isotopolog concentrations in enriched deuterated hydrogen gases.

The current uncertainty is mainly limited by the pressure and temperature measurements in the experiment and the relativistic effect in the calculation. Further improvements will allow for a primary refractive-index gas metrology with 10^{-6} accuracy. By taking into account the relativistic and QED corrections to the α^4 level, the polarizability of H_2 could be calculated to sub-ppm accuracy. At this stage, the comparison with experimental measurements will provide a stringent test of QED effects through means other than energy levels in such a four-body system.

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