

REFERENCE MEASUREMENTS OF HYDROGEN'S DIELECTRIC PERMITTIVITY

Eric F. May^{1,2,*}, Michael R. Moldover¹, James W. Schmidt¹

ABSTRACT

We used a quasi-spherical cavity resonator to measure the relative dielectric permittivity ϵ_r of H_2 at frequencies from 2.4 GHz to 7.3 GHz, at pressures up to 6.5 MPa, and at the temperatures 273 K and 293 K. The resonator was calibrated using auxiliary measurements of $\epsilon_r(p,T)$ for helium together with the accurate *ab initio* values of helium's dielectric permittivity. The measurements determine accurate values of hydrogen's molecular electric polarizability and its temperature dependence. At 273 K, we obtained $\alpha_e^{\text{H}_2} = (8.9568 \pm 0.0008) \times 10^{-41} \text{ F m}^2$ (all uncertainties reported here are one standard uncertainty), which agrees with the value $(8.9566 \pm 0.0026) \times 10^{-41} \text{ F m}^2$ that was obtained by combining Rychlewski's *ab initio* calculations with estimates of rotational level populations. Our results yield the temperature dependence $d\alpha_e^{\text{H}_2}/dT = \alpha_e^{\text{H}_2} \times (1.1 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$, which agrees with the calculated value $1.0 \times 10^{-5} \text{ K}^{-1}$. Our data also determine hydrogen's second dielectric virial coefficient, $b_\epsilon^{\text{H}_2} = (0.03 \pm 0.05) \text{ cm}^3 \text{ mol}^{-1}$, a property that has not yet been calculated.

1. Process Measurement Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8360, U.S.A.

2. Centre for Petroleum, Fuels & Energy, School of Mechanical Engineering, The University of Western Australia, Crawley WA 6009, Australia.

* Corresponding Author: Eric.May@uwa.edu.au

1. INTRODUCTION

The electromagnetic properties of an isotropic medium are characterized by its relative dielectric permittivity ϵ_r and its relative magnetic permeability μ_r . These quantities are defined in terms of the constitutive relations between the four vector fields present in the conventional form of Maxwell's equations [1]. For gases such as H₂, an accurate knowledge of ϵ_r and μ_r and their dependence on temperature T and pressure p is useful from both fundamental and applied perspectives. For example, measurements of hydrogen's refractive index $n \equiv \sqrt{\epsilon_r \mu_r}$ at microwave frequencies might be useful for monitoring the quantity of hydrogen in the fuel tank of a hydrogen powered vehicle. Such a monitor might accurately determine the mass of hydrogen in a tank even if temperature gradients were present because a microwave field detects a weighted average of n^2 over the volume of a tank and n^2 is a function of the density. From a fundamental standpoint, the uncertainty of many recently calculated properties of molecular hydrogen is comparable to the uncertainty achieved in their measurement. [2,3] Thus, a stimulating tension now exists between theory and accurate measurements of hydrogen's properties. In this work we compare accurate calculations of hydrogen's temperature-dependent molecular polarizability α_e with our accurate measurements of this property. We also estimate normal hydrogen's second dielectric virial coefficient b_ϵ , which contains information about the effect of pair interactions on electric polarizability. Dielectric virial coefficients have been calculated for atoms such as helium and argon [4, 5] and the CO–Ar van der Waals complex [6]; however, we are unaware of any such calculations for pairs of molecules.

In reference 7 we reported measurements of $\epsilon_r(p, T)$ and $n^2(p, T)$ for O₂ using a cross capacitor and a quasi-spherical resonator. For the present measurements, we used the same apparatus, which is shown schematically in Figure 1, to simultaneously determine ϵ_r (from measured capacitance ratios) and n^2 (from measured frequency ratios squared) for normal hydrogen. These two instruments were developed at NIST [8, 9] as part of a research program to measure $\epsilon_r(p, T)$ and/or $n^2(p, T)$ for helium as accurately as possible for use as a standard of pressure. Today, the uncertainty of the measurements of $\epsilon_r(p, T)$ and $n^2(p, T)$ for low-density helium exceeds that of recent *ab initio* calculations [10]; therefore we have used the calculated values as standards in

this work. We determined the compressibility of the capacitor and of the cavity resonator by calibration measurements using helium. Therefore, the present measurements of hydrogen's electric polarizability are made relative to helium's *ab initio* properties.

In contrast with paramagnetic O₂, both He and H₂ are diamagnetic (i.e. $\mu_r - 1 \cong 0$, $\mu_r < 1$) and, for these gases, the difference between $\varepsilon_r(p, T)$ and $n^2(p, T)$ is smaller than we can measure. Our values of $\varepsilon_r(p, T)$ for H₂ measured with the capacitor differed from the values of $n^2(p, T)$ measured with the quasi-spherical resonator by less than 2×10^{-6} , which is within the capacitor's uncertainty. Since the resonator values of $n^2(p, T)$ had approximately 1/10th of the uncertainty of the capacitor values of $\varepsilon_r(p, T)$, the results for H₂ reported below are those obtained by using calculated values of $\mu_r(p, T)$ to correct the measured values of $n^2(p, T)$. As described in Section 2, the magnitude of this correction was at most 1.4×10^{-7} , which is smaller than the estimated uncertainty of the n^2 values measured for H₂ with the resonator (discussed in Section 4).

In Section 2, the theory relating $\varepsilon_r(p, T)$ and $n^2(p, T)$ to α_e and b_e is described briefly. Differences between the methods described in reference 7 and those used for this work are discussed in Section 3. Experimental results and uncertainty estimates are discussed in Section 4, while the analysis of the results is presented in Section 5, as are comparisons with the results of *ab initio* calculations.

2. THEORY

The molar polarizability, \wp , of non-polar or weakly-polar fluids is related to ε_r and the molar density ρ via the Clausius-Mossotti equation [1]. For many fluids, \wp is a weak function of density, changing by only several percent between the vapor and liquid states; if so, the molar polarizability can be represented by the virial-type expansion

$$\wp = \frac{1}{\rho} \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \right) = A_\varepsilon (1 + b_\varepsilon \rho + c_\varepsilon \rho^2) \quad . \quad (1)$$

In Eq. (1), A_ϵ is the fluid's molar polarizability in the limit of zero density, while b_ϵ and c_ϵ are the second and third dielectric virial coefficients, respectively. In principle, these three macroscopic quantities can be calculated from quantum mechanics and statistical mechanics. For example, b_ϵ can be calculated from the intermolecular pair potential and the polarizability induced by the pair-wise interaction, while c_ϵ can be calculated by considering the effect of three-body interactions on the polarizability. However, the molar polarizability is dominated by A_ϵ , which is a property of a single molecule.

$$A_\epsilon = \frac{N_A}{3\epsilon_0} \left(\alpha_e(T) + \frac{\mu_e^2}{3k_B T} \right) \quad (2)$$

Here, N_A is the Avagadro constant, ϵ_0 is the electric constant, k_B is the Boltzmann constant, and μ_e is the molecule's electric dipole moment, which is zero for H_2 . Rychlewski [11] calculated *ab initio* the polarizability of the hydrogen molecule and its dependence on rotation and vibration. The higher rotational states of H_2 are centrifugally stretched and more polarizable than the ground state with zero total angular momentum. Therefore, the molecule's spin affects the value of α_e ; para-hydrogen (p - H_2) can access only states with even values of the quantum number J , whereas ortho-hydrogen is subject to odd values. For the mixture of para- and ortho-hydrogen known as normal hydrogen (n - H_2), Rychlewski calculated an effective value of α_e by taking an average over the rotational states $J = 0$ to 5 in the ground vibrational state. At 293 K his result is $\alpha_e = 8.958 \times 10^{-41} \text{ F m}^2$, corresponding to $A_\epsilon = 2.0309 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. This value is 0.25 % larger than the value $\alpha_e = 8.981 \times 10^{-41} \text{ F m}^2$ recommended by Maryott and Buckley [12] for H_2 at 293 K and 1 atm (1 atm = 101.325 kPa) based on measurements at radio, microwave, and optical frequencies. The relative uncertainty of Rychlewski's values of α_e for H_2 is estimated to be about 0.03 % because the calculation omits so-called nonadiabatic contributions to the molecule's polarizability [11,13]. We are unaware of any subsequent significant improvements upon Rychlewski's calculation of α_e for an isolated H_2 molecule.

Harvey and Lemmon [14] developed correlations for the dielectric constants of n - H_2 and p - H_2 as a function of temperature and density. Due to the scarcity of reliable experimental dielectric data

for H₂ at low densities, Harvey and Lemmon used Rychlewski's calculations of α_e , together with spectroscopic data to estimate the populations of various rotational states as a function of temperature, to determine A_ϵ for n -H₂ and p -H₂. At 273.16 K, by taking a population-weighted average over the rotational states $J = 0$ to 11 in the ground vibrational state [13] they found that n -H₂ has an effective value of $\alpha_e = (8.9566 \pm 0.0026) \times 10^{-41}$ F m², which is about 0.05 % larger than the effective value for p -H₂. The uncertainty bound represents the small (~ 0.03 %) non-adiabatic contributions omitted from Rychlewski's calculation but estimated in Table 5 of reference 11.

The density dependent terms in Harvey and Lemmon's correlations for the $\epsilon_r(p, T)$ of n -H₂ and p -H₂ were obtained from the low-temperature, high-density measurements of p -H₂ by Stewart [15]. (The high-density dielectric constant data of Michels et al [16] for n -H₂ were not used to develop the correlation in reference 14 because: (1) the data of Stewart lead to values of A_ϵ within 0.02 % of the calculated values for p -H₂ whereas the data of Michels et al are systematically lower by about 1 %, and (2) it can be argued that the higher dielectric virials should be largely independent of spin state [13].)

The dielectric permittivity can be deduced from measurements of the refractive index if the magnetic permeability is either known or negligibly different from one. The magnetic permeability of a gas may be estimated from the properties of a single molecule via the expansion

$$\frac{1}{\rho} \left(\frac{\mu_r - 1}{\mu_r + 2} \right) \cong A_\mu = \frac{N_A \mu_0}{3} \left(\alpha_m(T) + \frac{\mu_m^2}{3k_B T} \right) . \quad (3)$$

Here, A_μ is the fluid's molar magnetizability in the limit of zero density, $\mu_0 \equiv 4\pi \times 10^{-7}$ N A⁻² is the magnetic constant, α_m is the molecular magnetizability and μ_m is the molecule's magnetic dipole moment, which is zero for H₂. The molecular magnetizability consists of a diamagnetic component and a "high-frequency" component, which accounts for the contribution to the static magnetizability from transitions between molecular states which have energies comparable to or

larger than $k_B T$. For H_2 only the latter has been measured directly [17]; however it is the diamagnetic contribution that dominates. Rychlewski and Raynes [18] calculated both components of α_m for H_2 and their dependence on rotation and vibration. For an H_2 molecule at its equilibrium internuclear separation of 1.4 Bohr radii (0.74×10^{-10} m), their result is $A_\mu = N_A \mu_0 \alpha_m / 3 = -1.7 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$.

We combine Eq. (2) and Eq. (3) to estimate n^2/ε

$$\frac{n^2}{\varepsilon} \approx \frac{1 + (A_\varepsilon + A_\mu)\rho}{1 + A_\varepsilon\rho} \approx 1 + A_\mu\rho. \quad (4)$$

In Eq. (4), we used $\rho(p, T)$ from equation of state for $n\text{-}H_2$ of Leachman et al. [19], as implemented in the software REFPROP 8.0 [20], to correct the values of n^2 measured with the resonator to values of $\varepsilon_r(p, T)$. The maximum value of $|A_\mu\rho|$ was 1.34×10^{-7} and its average value was 6.5×10^{-8} . This correction was approximately as large as the repeatability of the resonator measurements: 1×10^{-7} . (See Section 4.2 and reference 7.)

3. APPARATUS AND MEASUREMENTS

Figure 1 is a conceptual diagram of the apparatus. The capacitor and the microwave cavity were surrounded by independent pressure vessels; however, both pressure vessels were immersed in the same thermostatted, stirred-liquid bath and both pressure vessels were connected to the same gas supply and pressure balance. This ensured that ε_r and n were measured at nearly identical temperatures and pressures despite small fluctuations of the temperature and the pressure. A thorough description of the methods used in this experiment is given in May et al. [7] and in the sections below we describe only those features of the current methods that differed from the description given previously.

3.1. The resonator and capacitor

Capacitances were measured using an automated three-wire bridge at a frequency of 2 kHz, and a vector-network analyzer linked to a rubidium clock was used to measure four modes of the cavity resonator at frequencies of 2.6, 4.3, 5.8 and 7.2 GHz. The working equations for

converting the measured capacitance ratios and frequency ratios to values of ε_r and n^2 require knowledge of only two parameters per apparatus: its effective isothermal compressibility k_T and the vacuum capacitance or frequency. (For the resonator, the vacuum frequency of each mode was required.) As described in reference 7, the apparatus parameters were determined by calibration with helium; however, unlike O_2 , the absorption of microwaves by H_2 is negligible. Therefore we determined $n_{He}^2(p, T)$ and $n_{H_2}^2(p, T)$ from the purely real expression [9]:

$$n^2(p, T) = \left(\frac{\langle f_{vac} + g_{vac} \rangle_{ln}^\sigma}{\langle f + g \rangle_{ln}^\sigma (1 - k_{T, res} p/3)} \right)^2 \quad (5)$$

Here, $k_{T, res}$ is the resonator's isothermal compressibility, the superscript $\sigma = TM$ or TE denotes the mode type, which are also enumerated by the indices l and n , f_{vac} and g_{vac} are the mode's vacuum resonance frequency and half-width, and the angled brackets denote an average over the three components of each $l = 1$ mode. The apparatus parameters $\langle f + g_{vac} \rangle_{ln}^\sigma$ and $k_{T, res}$ were determined from isothermal helium measurements by adjusting their values in Eq. (5) to obtain optimal agreement with values of $n_{He}^2(p, T)$ calculated from theory, as described in Section 4.1.

The average frequency of any triplet of modes could be determined with a fractional uncertainty of approximately 4×10^{-9} . However, at the highest hydrogen density, the average frequency typically varied by a factor of 5×10^{-8} during a half hour. This variation corresponds to a temperature drift of 1 mK or a pressure drift of 20 Pa.

3.2. Temperature, Pressure and Gas Purity

The supplier of the hydrogen used in this work stated that its purity was 99.9999 % by volume. The supplier of the helium stated that its purity was 99.9999 % by volume, and that it had a water content of less than 0.2 ppm. Typically, data along isotherms were taken in order of increasing pressure from around 0.1 MPa to about 6.5 MPa in steps of either 0.5 or 1 MPa, and then in decreasing steps of the same size. For both helium and hydrogen, we allowed 2.5 hours for equilibration following a change in pressure; after this amount of time, all of the readings reached steady values.

Under steady state conditions, the temperature of the stirred oil bath, the pressure vessels immersed in the bath, and the resonator and the capacitor contained in the pressure vessels were all assumed to be equal. The bath temperature was measured with a calibrated standard platinum resistance thermometer and we estimate that the temperature uncertainty was 5 mK with respect to ITS-90, the international temperature scale of 1990. The helium and the hydrogen measurements were made along two isotherms: 273.203 K and 293.213 K. In the remainder of this paper, these isotherms will be referred to by their nearest integer temperatures: 273 K and 293 K. (Measurements at 323 K were attempted but unfortunately a pressure transducer failure prevented us from completing them or from obtaining reliable data at that temperature.)

Gas pressure was monitored by a quartz-crystal pressure transducer located above the oil bath. The full scale of this transducer was 7 MPa. The transducer was calibrated over the range 0 to 7 MPa against a piston gage which was in turn calibrated against one of the primary pressure standards at NIST. Based on these calibrations, we estimate the uncertainty of the pressure measurements reported here to be less than 0.1 kPa.

4. RESULTS

Effectively, we determined $\varepsilon_{r,\text{H}_2}(p,T)$ and $n_{\text{H}_2}^2(p,T)$ from the *ab initio* properties of helium and measurements of the ratios $\varepsilon_{r,\text{H}_2}(p,T)/\varepsilon_{r,\text{He}}(p,T)$ and $n_{\text{H}_2}^2(p,T)/n_{\text{He}}^2(p,T)$. The measurement uncertainty for these ratios does not depend directly on the total uncertainties of our pressure and temperature measurements. Rather it is the stability of the apparatus calibrations over the duration of the hydrogen measurements, together with the repeatability of the hydrogen measurements, which determines the uncertainty of the ratios. We checked the stability of the resonator and capacitor by making helium measurements before and after the hydrogen measurements at 273 K and 293 K.

4.1. Helium Measurements

The apparatus parameters were determined at each temperature by regression of the measured capacitance and frequency ratios to values of $\varepsilon_{r,\text{He}}(p,T)$ and $n_{\text{He}}^2(p,T)$ determined from *ab initio* calculations of $\rho_{\text{He}}(p,T)$, $\varepsilon_{r,\text{He}}(\rho,T)$ and $\mu_{r,\text{He}}(\rho)$ as described by Schmidt et al [10].

The results agree with those reported in reference 7, within the combined statistical uncertainties of the best-fit apparatus parameter values. We exploited the more accurate calculations of $\rho_{\text{He}}(p, T)$ that have been completed since the references in [7] and [10]. Specifically, we used Hurly and Mehl's [21] values of the second density virial coefficient $B(T)$ and Garberoglio and Harvey's [22] values of the third density coefficient $C(T)$. We obtained the values $(813 \pm 10) \text{ cm}^3 \text{ mol}^{-3}$ at 273 K and $(700 \pm 20) \text{ cm}^3 \text{ mol}^{-3}$ at 323 K for the fourth virial coefficient by reanalyzing the data of Blancett et al [23] using these values of $B(T)$ and $C(T)$ and their uncertainties as constraints. (The value of $D(293 \text{ K})$ used to analyze the helium data measured at that temperature was obtained by linear interpolation.) The uncertainty of $B(T)$ and some of the uncertainty of $C(T)$ result from the uncertainty of the He-He inter-atomic potential; thus, they are partially correlated (depending on the relative magnitudes of the three-body potential and the pair potential). We estimated that the fractional uncertainty of $\rho_{\text{He}}(p, T)$ calculated from $B(T)$, $C(T)$, and $D(T)$ is 1.0×10^{-5} at 2700 mol m^{-3} , the highest density of our measurements. This corresponds to the maximum uncertainty $u[\varepsilon_{r, \text{He}}(p, T)] = 4 \times 10^{-8}$.

The stability of the apparatus parameters was different at each temperature. We deduced it from the values of the vacuum cross-capacitance $C_{x, \text{vac}}$ and the average $\langle f_{\text{vac}} + g_{\text{vac}} \rangle_{1n}^{\sigma}$ determined from the helium measurements before and after the hydrogen measurements. Averaged over all modes, the fractional change in $\langle f_{\text{vac}} + g_{\text{vac}} \rangle_{1n}^{\sigma}$ at 273 K and 293 K was $+2 \times 10^{-8}$ and $+1.3 \times 10^{-7}$, respectively, which is comparable to the drifts observed in reference 7. However, the fractional change in $C_{x, \text{vac}}$ at 273 K and 293 K was $+6.0 \times 10^{-6}$ and $+1.2 \times 10^{-6}$, respectively, which is significantly larger than observed in reference 7. When the hydrogen data were analyzed, we used values of $C_{x, \text{vac}}$ and $\langle f_{\text{vac}} + g_{\text{vac}} \rangle_{1n}^{\sigma}$ that were interpolated linearly as a function of time between the two values determined from the helium measurements.

The isothermal capacitance and frequency data were also regressed to the polynomial functions

$$\frac{C_x}{C_{x, \text{vac}}} = 1 + \sum_{i=1}^3 a_i \left(\frac{P}{RT} \right)^i \quad (6a)$$

$$\frac{\langle f + g \rangle_{ln}^\sigma}{\langle f_{vac} + g_{vac} \rangle_{ln}^\sigma} = 1 + \sum_{i=1}^3 d_i \left(\frac{P}{RT} \right)^i = \frac{1}{n_{fit}}. \quad (6b)$$

Here C_x is the measured cross capacitance, and each of the parameters a_i and d_i were tested for statistical significance. One purpose of these regressions was to estimate the scatter of the data for each isotherm about the curve $\varepsilon_{r,fit}(p/RT) = n_{fit}^2 / \mu_r$. The deviations of our ε_r data from $\varepsilon_{r,fit}$ for both helium and hydrogen are shown in Figure 2. Another reason for the regression is the relation $a_1 = 3(A_\varepsilon - k_{T,cap}RT/9)$, for the parameter in Eq. (6a) where $k_{T,cap}$ is the isothermal compressibility of the capacitor [8]. Thus, the difference between the parameters a_1^{H2} and a_1^{He} determined by regression of Eq. (6a) to $C_x(p)$ data for hydrogen and helium, respectively, allows the determination of $A_\varepsilon^{H2} - A_\varepsilon^{He}$ without reference to either $k_{T,cap}$ or to an equation of state.

$$A_\varepsilon^{H2} = A_\varepsilon^{He} + (a_1^{H2} - a_1^{He})/3 \quad (7)$$

A similar equation can be derived for the difference between d_1^{H2} and d_1^{He}

$$A_\varepsilon^{H2} + A_\mu^{H2} = A_\varepsilon^{He} + A_\mu^{He} - 2(d_1^{H2} - d_1^{He})/3 \quad (8)$$

The magnetic polarizabilities A_μ^{H2} and A_μ^{He} are 8×10^{-6} and 4×10^{-6} times smaller than A_ε^{H2} , respectively, and can be neglected. Since A_ε^{He} has been calculated *ab initio* by Lach et al [24] with a relative uncertainty of 2×10^{-7} , the precision of A_ε^{H2} determined with Eq. (8) is limited by the relative uncertainty of $d_1^{H2} - d_1^{He}$, which for our data was 4×10^{-5} . The results of these determinations are discussed in Section 5

4.2. Hydrogen Measurements

The n_{H2}^2 data obtained with the resonator were converted to $\varepsilon_{r,H2}$ using values of $\mu_{r,H2}$ as described in Section 2. No frequency dependence in $\varepsilon_{r,H2}$ was detectable: the standard deviation

of the permittivity values from each of the resonator's four modes had a maximum of 0.5×10^{-7} , and the standard deviation of the difference between $\varepsilon_{r,\text{H}_2}$ determined by the capacitor and the resonator was 8.7×10^{-7} . This last value is smaller than the manufacturer's specification for the non-linearity of the capacitance bridge (1×10^{-6}). Thus, the values of $\varepsilon_{r,\text{H}_2}$ listed in Table 1 and discussed below are those obtained from measurements with the resonator.

The standard deviations of $(\varepsilon_r - \varepsilon_{r,\text{fit}})$ for hydrogen were $(0.7 \text{ and } 0.2) \times 10^{-7}$ on the isotherms at 273 K and 293 K, respectively. The deviations were not random; they resulted almost entirely from hysteresis in the frequencies measured with increasing and decreasing pressure. This hysteresis in the frequency ratios was approximately five times larger for hydrogen than for helium, which is larger than the polarizability ratio (≈ 3.9) of the two gases. This suggests that the long-term temperature drift in the resonator was slightly larger for the hydrogen measurements than for the helium measurements.

Based on the standard uncertainties of the polynomial fits to the helium and hydrogen data, the estimated average standard uncertainties of the ratio $\varepsilon_{r,\text{H}_2}(p,T)/\varepsilon_{r,\text{He}}(p,T)$ determined with the resonator is 1×10^{-7} . (This ratio may be determined by first calculating $\varepsilon_{r,\text{He}}(p,T)$ using the method described in Schmidt et al. [10] at the each of the pressures and temperatures listed in Table 1.) However, the uncertainties of the $\varepsilon_{r,\text{H}_2}(p,T)$ values listed in Table 1 are dominated by the temperature and pressure uncertainties. The temperature uncertainty $u(T) = 0.005 \text{ K}$ corresponds to the uncertainty of the dielectric constant of hydrogen $u(\varepsilon_{r,\text{H}_2}) = [1.7 + 2.7 \times (293 \text{ K}/T) (p/6 \text{ MPa})] \times 10^{-7}$. The pressure uncertainty $u(p) = 0.1 \text{ kPa}$ corresponds to the uncertainty $u(\varepsilon_{r,\text{H}_2}) = 2.6 \times 10^{-7} (293 \text{ K}/T)$. Combining these in quadrature, the total uncertainty of $\varepsilon_{r,\text{H}_2}$ is 3.4×10^{-7} at 293 K and 3 MPa.

Figure 3 compares the dielectric permittivities listed in Table 1 with values calculated using the correlation of Harvey and Lemmon [14] as implemented in the software REFPROP 8.0 [20]. All

the deviations have a magnitude less than 0.9×10^{-6} ; their average is $+0.3 \times 10^{-6}$ and their standard deviation is $+0.2 \times 10^{-6}$.

5. DISCUSSION

Experimental values for α_e , $d\alpha_e^{\text{H}_2}/dT$ and b_ε for hydrogen can be extracted from our data. The primary purpose of extracting these quantities is to test and stimulate theory; α_e and $d\alpha_e^{\text{H}_2}/dT$ have already been calculated *ab initio* by Rychelwski [11], and Rizzo [25] has suggested a method by which the *ab initio* calculation of b_ε for hydrogen might proceed. We used two methods (referred to as Method 1 and Method 2) to extract these quantities from our data because each of the methods has a different problem associated with it, as discussed below. Nevertheless, the two methods give similar results and the values of α_e , $d\alpha_e^{\text{H}_2}/dT$ and b_ε that we ultimately recommend are the weighted averages of the values obtained with the two methods.

Method 1 is based on the correlation

$$\frac{\varepsilon_r^{\text{calc}} - 1}{\varepsilon_r^{\text{calc}} + 2} = A_{\varepsilon, 273\text{K}} \rho (1 + b_\varepsilon \rho + c_\varepsilon \rho^2) + A_\tau \rho \left(\frac{T}{273.16\text{K}} - 1 \right), \quad (9)$$

which Schmidt and Moldover [8] used to describe their measurements of the dielectric permittivities of eight gases. Method 1 is optimized for representing our measured ε_r data as a function of pressure and temperature; however the values of α_e , $d\alpha_e^{\text{H}_2}/dT$ and b_ε obtained with Method 1 are sensitive to the choice of the equation of state used to calculate molar densities from the measured temperature and pressure. In Eq. (9), $A_{\varepsilon, 273\text{K}}$ is the value of A_ε at 273.16 K, and A_τ is a parameter that accounts for the small temperature dependence of A_ε associated with ‘centrifugal stretching’ in diatomic molecules. All the data in Table 1 were fit to Eq. (9) using densities from refs. 19 and 20. The parameter c_ε was not statistically significant so the fit was repeated with $c_\varepsilon \equiv 0$. The best-fit parameter values, and their statistical uncertainties, obtained

with this fit were $A_{\epsilon, 273\text{K}} = 2.03075 \pm 0.00001 \text{ cm}^3 \text{ mol}^{-1}$, $b_{\epsilon} = 0.0636 \pm 0.0015 \text{ cm}^3 \text{ mol}^{-1}$, and $A_{\tau} = 0.00599 \pm 0.00017 \text{ cm}^3 \text{ mol}^{-1}$.

However, as discussed in reference 7, the best-fit values of the parameters in Eq. (9) are sensitive to three choices: (1) the total number of parameters allowed to vary during the regression, (2) the choice of the equation of state used to convert the measured p and T to ρ , and (3) the details of the objective function minimized by the regression. For example, if the equation of state is changed from that of Leachman et al [19] to that of Kunz et al [26], the resulting values of $A_{\epsilon, 273\text{K}}$, b_{ϵ} and A_{τ} are $2.03042 \pm 0.00001 \text{ cm}^3 \text{ mol}^{-1}$, $0.0650 \pm 0.0019 \text{ cm}^3 \text{ mol}^{-1}$ and $0.00627 \pm 0.00017 \text{ cm}^3 \text{ mol}^{-1}$, respectively. Thus the uncertainty of the values of $A_{\epsilon, 273\text{K}}$, b_{ϵ} and A_{τ} (and the corresponding values of α_{ϵ} and $d\alpha_{\epsilon}^{\text{H}_2}/dT$) obtained with this method are dominated by the choices enumerated above.

The second method does not make use of an equation of state and treats each set of isothermal data independently before combining the results to obtain average values of α_{ϵ} , $d\alpha_{\epsilon}^{\text{H}_2}/dT$, and b_{ϵ} for the temperature range 273 K to 293 K. Method 2 uses the best-fit polynomial parameters d_i in Eq. (6b) determined for hydrogen and helium. First, the polynomial parameters d_i determined for our hydrogen and helium data at each temperature are used in used Eq. (8), together with the *ab initio* value of $A_{\epsilon}^{\text{He}} = 0.51725419 \text{ cm}^3 \text{ mol}^{-1}$ [24], to obtain $A_{\epsilon, 273\text{K}}^{\text{H}_2} = 2.0307 \pm 0.0001 \text{ cm}^3 \text{ mol}^{-1}$ and $A_{\epsilon, 293\text{K}}^{\text{H}_2} = 2.0311 \pm 0.0001 \text{ cm}^3 \text{ mol}^{-1}$. The difference between $A_{\epsilon, 293\text{K}}^{\text{H}_2}$ and $A_{\epsilon, 273\text{K}}^{\text{H}_2}$ provides the estimate $A_{\tau} = 0.0061 \pm 0.0014 \text{ cm}^3 \text{ mol}^{-1}$. Figure 4 shows a comparison of several determinations of A_{ϵ} for normal hydrogen over the temperature range 273 K to 323 K. The top panel shows the two values we obtained with Method 2 together with the experimental values determined by Orcutt and Cole [27], with a capacitance based expansion-type apparatus, and by Newell and Baird [28] with a microwave resonant cavity. The solid line represents our recommended values of $A_{\epsilon, 273\text{K}}^{\text{H}_2}$ and A_{τ} , obtained from the weighted average the results from Methods 1 and 2 (discussed below). The lower panel shows deviations between our recommended values of A_{ϵ} and values obtained with Method 1 using different

equations of state, with Method 2, and with the literature correlation of Harvey and Lemmon [14].

Estimates of b_ϵ at each measured temperature can also be obtained using Method 2 from the polynomial parameters d_i . Ignoring the small magnetic terms, the polynomial coefficient d_2 in Eq. (6b) is determined by the expression

$$d_2 = \frac{A_\epsilon}{8} \left(15A_\epsilon - 12 \left(\Delta b + \frac{k_{T,\text{res}} RT}{3} \right) \right). \quad (10)$$

Here, $\Delta b = b_\epsilon - B$, where B is the second density virial coefficient at the measurement temperature, and terms of order $(k_T RT / 3)^2$ or smaller have been dropped. Thus, the difference between the parameters $d_2^{\text{H}_2}$ and d_2^{He} determined by regression of Eq. (6b) to $\langle f + g \rangle_{\ln}^\sigma$ data for hydrogen and helium, respectively, allows the determination of $\Delta b^{\text{H}_2} - \Delta b^{\text{He}}$ without reference to the apparatus parameter $k_{T,\text{res}}$.

$$b_\epsilon^{\text{H}_2} = B_{\text{H}_2} + \frac{-8D_2 + 15(A_\epsilon^{\text{H}_2})^2 - 18A_\epsilon^{\text{H}_2} A_\epsilon^{\text{He}} + 3(A_\epsilon^{\text{He}})^2 + 12A_\epsilon^{\text{He}} \Delta b_{\text{He}}}{12A_\epsilon^{\text{H}_2}} \quad (11a)$$

where

$$D_2 = d_2^{\text{H}_2} - d_2^{\text{He}} + d_1^{\text{He}} (d_1^{\text{He}} - d_1^{\text{H}_2}) \quad (11b)$$

The values of $B_{\text{H}_2} - b_\epsilon^{\text{H}_2}$ calculated from our data, Eq. (6) and Eq. (11) were $(13.87 \pm 0.03) \text{ cm}^3 \text{ mol}^{-1}$ at 273 K and $(14.31 \pm 0.03) \text{ cm}^3 \text{ mol}^{-1}$ at 293 K. The uncertainties listed are those arising from the combination in quadrature of the statistical uncertainties of the best-fit values of $d_2^{\text{H}_2}$ and d_2^{He} . They do not include the uncertainties of the *ab initio* values of B_{He} from Hurly and Mehl [21] or the *ab initio* values of b_ϵ^{He} from Rizzo et al. [29]. To obtain $b_\epsilon^{\text{H}_2}$ at each temperature, we used the *ab initio* values of B_{H_2} from Patkowski et al. [2], who stated that the contribution to their uncertainty in their B_{H_2} values resulting from the convergence of their calculations was $\pm 0.03 \text{ cm}^3 \text{ mol}^{-1}$ at 273 K and 300 K. This is consistent with our estimate of

$\pm 0.04 \text{ cm}^3 \text{ mol}^{-1}$ based on the agreement between viscosities of $n\text{-H}_2$ calculated *ab initio* by Mehl et al. [3] using the potential of Patkowski et al. [2] and the experimental measurements reported by May et al. [30]. Importantly, these values of B_{H_2} are independent of the second virial coefficients calculated from the equation of state of Leachman et al. [19] or any other equation of state for normal hydrogen.

Figure 5 shows the values of $b_\epsilon^{\text{H}_2}$ obtained at both temperatures with Method 2, together with the (temperature-independent) values of $b_\epsilon^{\text{H}_2}$ obtained using Method 1 using different equations of state. Also shown is the value of $b_\epsilon^{\text{H}_2}$ measured at 322 K by Orcutt and Cole [27] and the temperature dependent $b_\epsilon^{\text{H}_2}$ used in the correlation of Harvey and Lemmon [14]. The weighted average and standard deviation of the $b_\epsilon^{\text{H}_2}$ values obtained from our data with Method 2 was $0.003 \text{ cm}^3 \text{ mol}^{-1}$ and $0.02 \text{ cm}^3 \text{ mol}^{-1}$, respectively.

Method 2 has problems resulting from the correlations among the best-fit values of d_i . Since ϵ_r is naturally a function of density, not pressure, the same data can be described by using fewer free parameters with Eq. (9) than with Eq. (8). Although the values of d_3 are statistically different from zero, there are insufficient high-density data to determine them reliably and specific values of each d_i are significantly correlated. Given that both Method 1 and Method 2 suffer from problems associated with correlation between regression parameters but that the correlations between the parameters used in Method 1 are independent of those in Method 2, the values of α_ϵ , $d\alpha_\epsilon^{\text{H}_2}/dT$ and b_ϵ we recommend were obtained from a weighted average of the results from the two methods. The uncertainty bound we assign to these recommended values encompasses the standard uncertainties obtained by each method. (Note: for the purpose of representing the $\epsilon_{r,\text{H}_2}(p,T)$ data listed in Table 1, we recommend the parameters obtained with Method 1 using the equation of state of Leachman et al [19].)

Thus, for the purpose of estimating the molecular properties of H_2 , we recommend $A_{\epsilon,273\text{K}}^{\text{H}_2} = 2.03065 \pm 0.00017 \text{ cm}^3 \text{ mol}^{-1}$ and $A_\tau = 0.0061 \pm 0.0014 \text{ cm}^3 \text{ mol}^{-1}$. Since hydrogen has no electric dipole moment, converting this recommended value of $A_{\epsilon,273\text{K}}^{\text{H}_2}$ to an effective

$\alpha_e^{\text{H}_2}$ using Eq. (2) gives $\alpha_e^{\text{H}_2} = (8.9568 \pm 0.0008) \times 10^{-41} \text{ F m}^2$. Within the experimental uncertainty, this agrees with the value $\alpha_e = (8.9566 \pm 0.0026) \times 10^{-41} \text{ F m}^2$ calculated by Harvey and Lemmon [14] using Rychlewski's *ab initio* results [11], as described in Section 2. The measured value of A_τ also agrees with the value $A_\tau = 0.0056 \text{ cm}^3 \text{ mol}^{-1}$ calculated by Harvey and Lemmon using Rychlewski's *ab initio* results, within the experimental uncertainty.

Combining the b_ϵ results obtained with Methods 1 and 2 leads us to recommend the value $b_\epsilon^{\text{H}_2} = 0.03 \pm 0.05 \text{ cm}^3 \text{ mol}^{-1}$ over the temperature range 273 to 293 K. Orcutt and Cole [27] used an expansion-type apparatus at 322 K to measure b_ϵ for several gases including H_2 and He without reference to the gas's equation of state or second density virial coefficient. Their measurement of b_ϵ^{He} is in excellent agreement with the value calculated *ab initio* by Rizzo et al. [29], and their value of $b_\epsilon^{\text{H}_2} = 0.03 \pm 0.10 \text{ cm}^3 \text{ mol}^{-1}$ is in remarkable agreement with ours. These two values of $b_\epsilon^{\text{H}_2}$ were obtained from measurements of *n*- H_2 ; they are slightly smaller than the value $0.09 \text{ cm}^3 \text{ mol}^{-1}$ obtained by Harvey and Lemmon [14] from Stewart's [15] measurements of *p*- H_2 at 15 times higher densities than those used here and at much lower temperatures (24 K to 100 K).

ACKNOWLEDGEMENTS

The authors thank John Hurly for his thermophysical property calculations, Jim Mehl and Allan Harvey for calculations of the *ab initio* values of hydrogen's second virial coefficient, and Laurent Pitre for assistance with the measurements. We thank Allan Harvey and Robert Berg for reading the manuscript and we appreciate their comments and suggestions. While at NIST, E.F.M. was supported in part by the American Australian Association.

TABLES

Table 1. Measured values of the relative dielectric permittivity of normal hydrogen.

T (K)	p (MPa)	$10^4(\epsilon_r - 1)$	T (K)	p (MPa)	$10^4(\epsilon_r - 1)$
273.203	0.14308	3.836	273.203	2.97775	78.628
273.203	0.50469	13.500	273.203	2.48108	65.684
273.203	1.01268	27.016	273.203	1.99505	52.952
273.203	1.50098	39.940	273.203	1.48246	39.454
273.203	2.00864	53.307	273.203	0.99251	26.483
273.203	2.50760	66.374	273.203	0.49393	13.216
273.203	2.99499	79.074	273.203	0.14833	3.979
273.203	3.49657	92.068	293.213	0.10278	2.564
273.203	4.00584	105.196	293.213	1.50175	37.249
273.203	4.49358	117.701	293.213	2.50700	61.869
273.203	4.98987	130.357	293.213	3.49981	85.938
273.204	5.48993	143.040	293.213	4.49224	109.754
273.203	5.98846	155.615	293.213	5.49163	133.491
273.204	6.24354	162.024	293.213	6.48849	156.925
273.203	5.98362	155.494	293.213	5.48687	133.380
273.203	5.50901	143.523	293.213	4.48967	109.695
273.203	4.98637	130.268	293.213	3.49671	85.865
273.203	4.50468	117.985	293.213	2.47428	61.073
273.203	3.98847	104.751	293.213	1.47972	36.706
273.203	3.49679	92.076	293.213	0.10867	2.711

FIGURES

Figure 1. Schematic diagram of the apparatus.

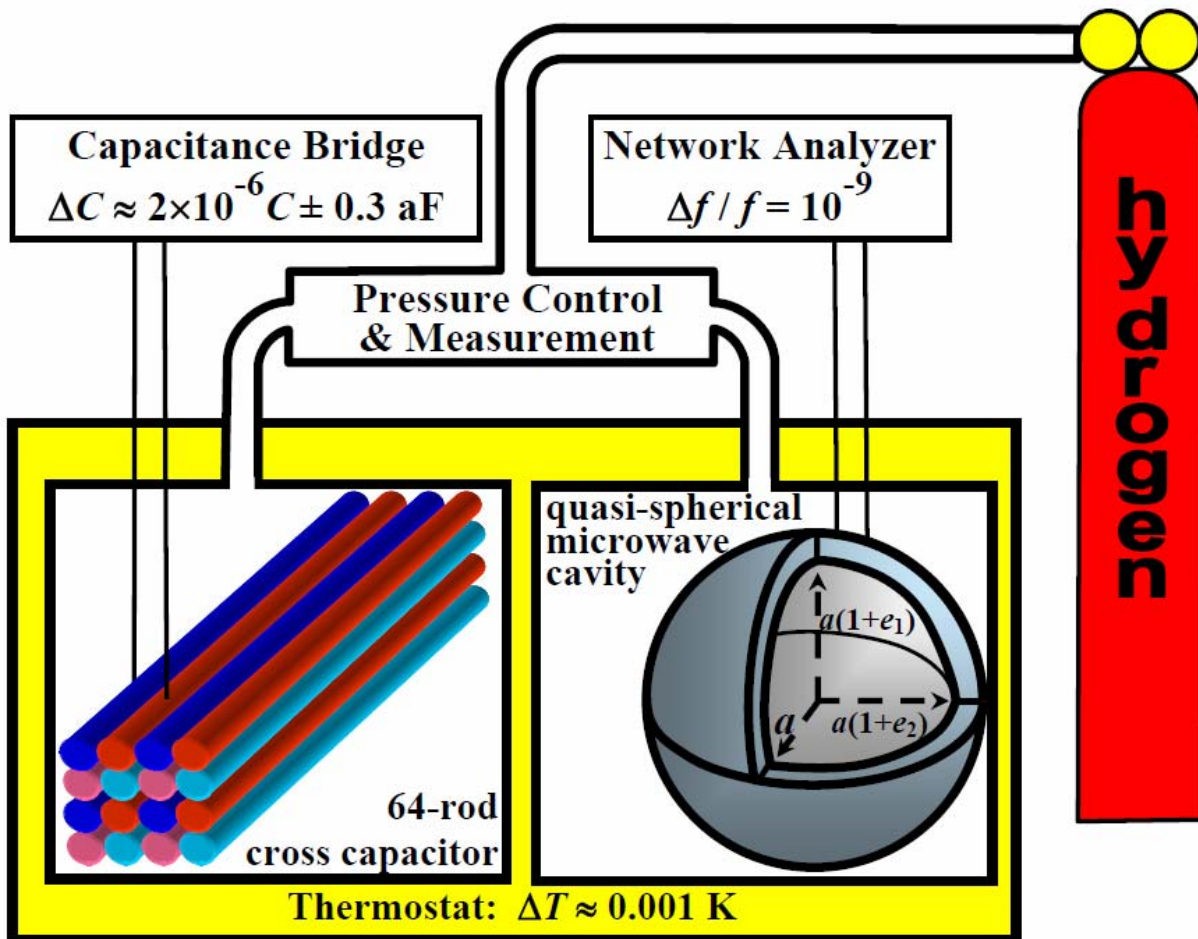


Figure 2. Deviations of our $\varepsilon_r(p, T)$ data for hydrogen (top panel) and helium (bottom panel) from the best-fit polynomials $\varepsilon_{r, \text{fit}}$ obtained by regression of Eq. (6b) to the measured isothermal frequency ratios. For each isotherm, data measured as the pressure was increased are shown together with data measured as the pressure was decreased.

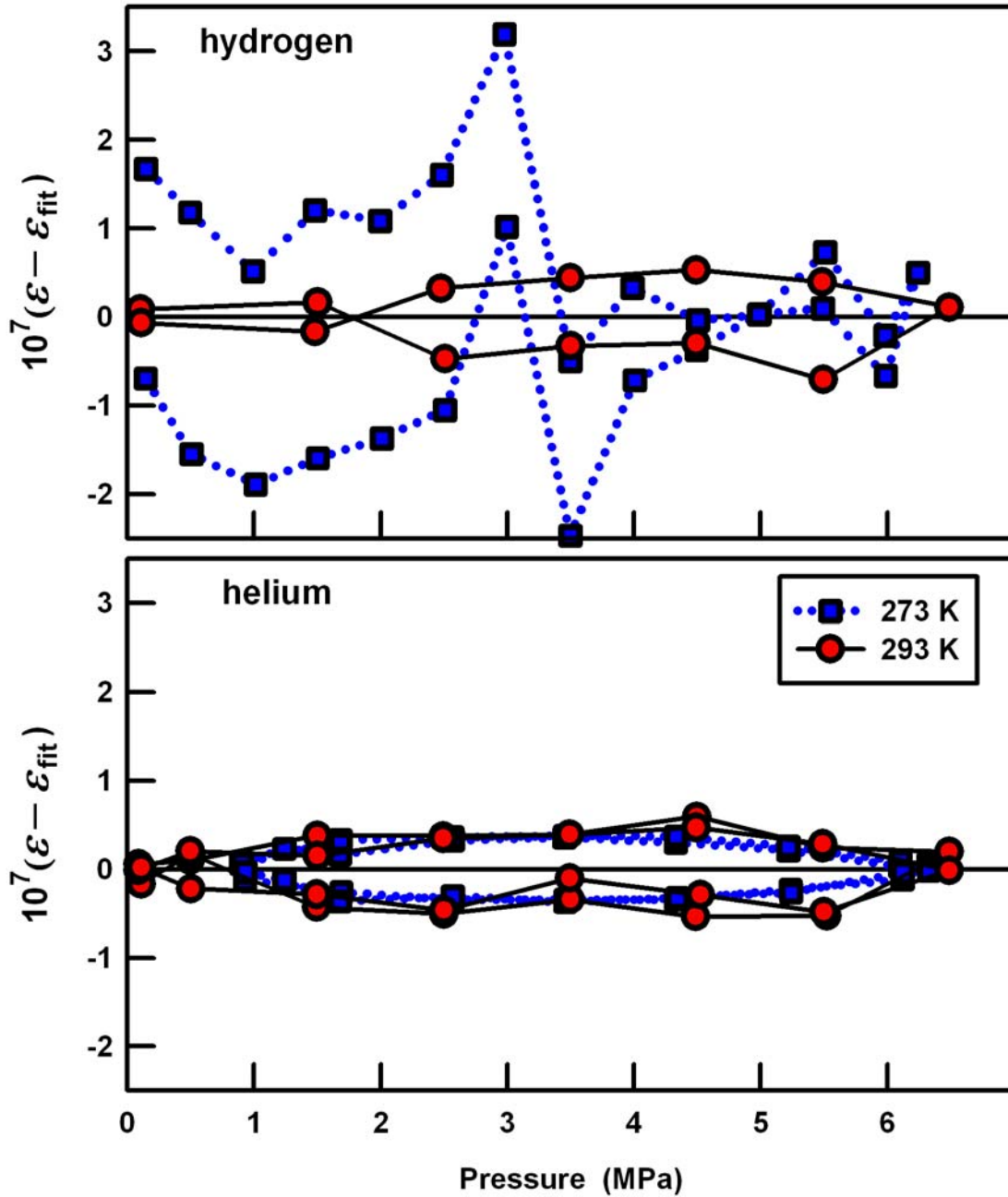


Figure 3. Differences between measured values of the dielectric permittivity of hydrogen, ϵ_{meas} , and values ϵ_{lit} calculated using literature references 14, 19 and 20. For each isotherm, data measured as the pressure was increased are shown together with data measured as the pressure was decreased.

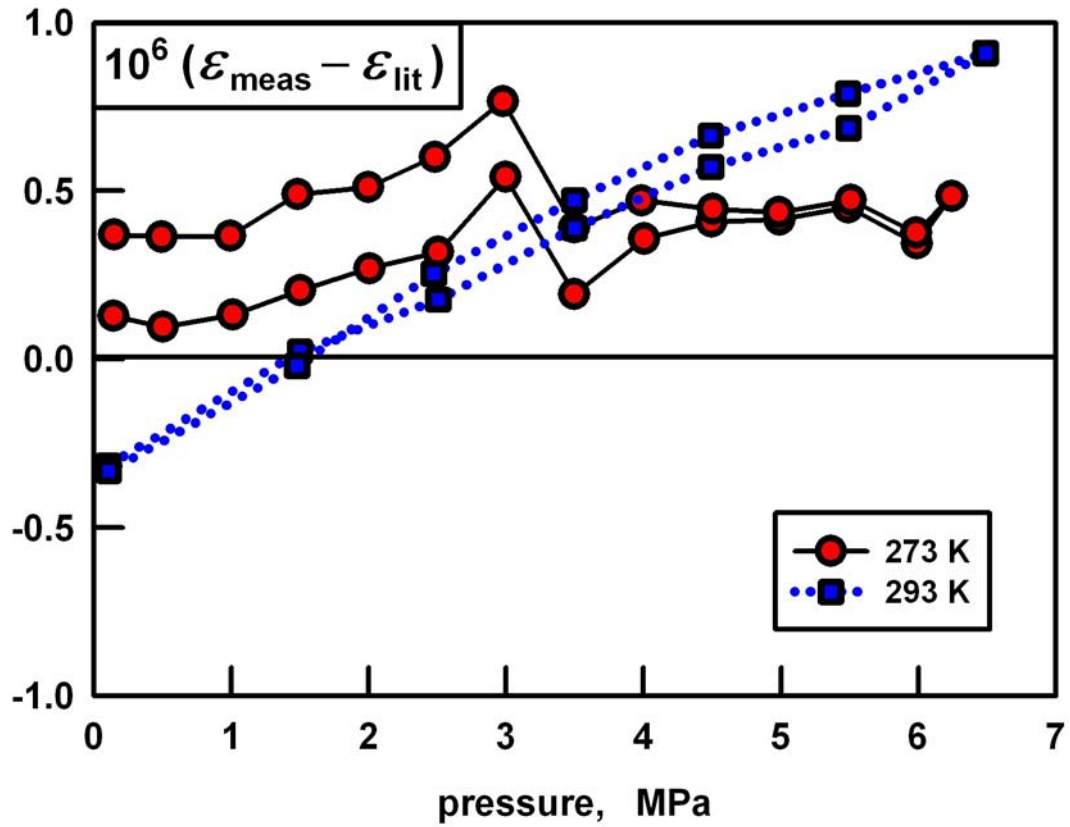


Figure 4. Temperature dependence of the molar polarizability of normal hydrogen in the limit of zero density A_ϵ . (a) Results from this work (Method 2 and the average of Methods 1 and 2), together with the A_ϵ values obtained from the measurements of Orcutt and Cole [27] and Newell and Baird [28]. (b) Deviations from the values of $A_{\epsilon,273K}^{H_2}$ and A_τ recommended in this work. The symbols show the deviations obtained using Method 1 (with either [19] or [26]) or using Method 2. The dashed line shows the deviation of the correlation reported in ref. 14.

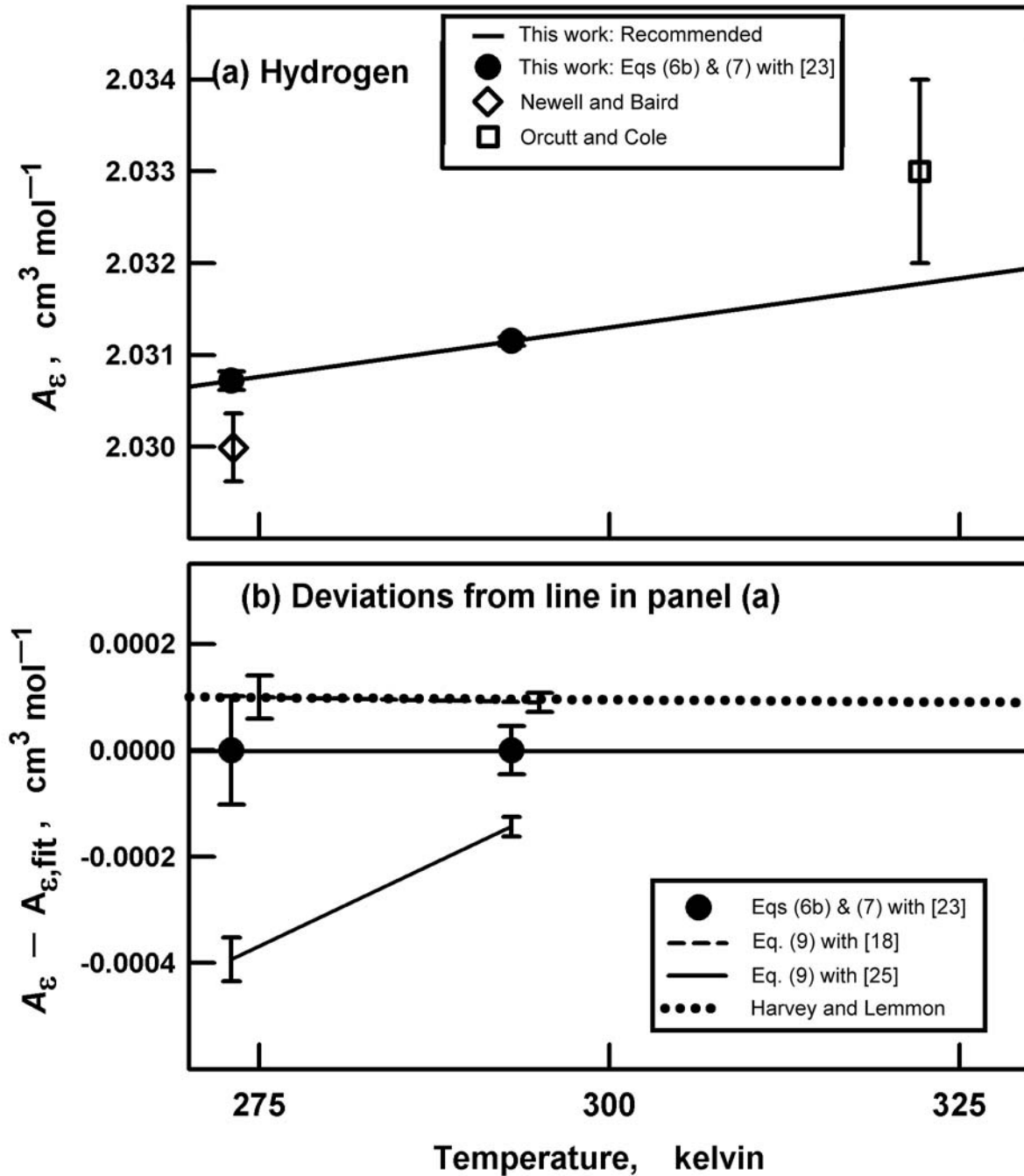
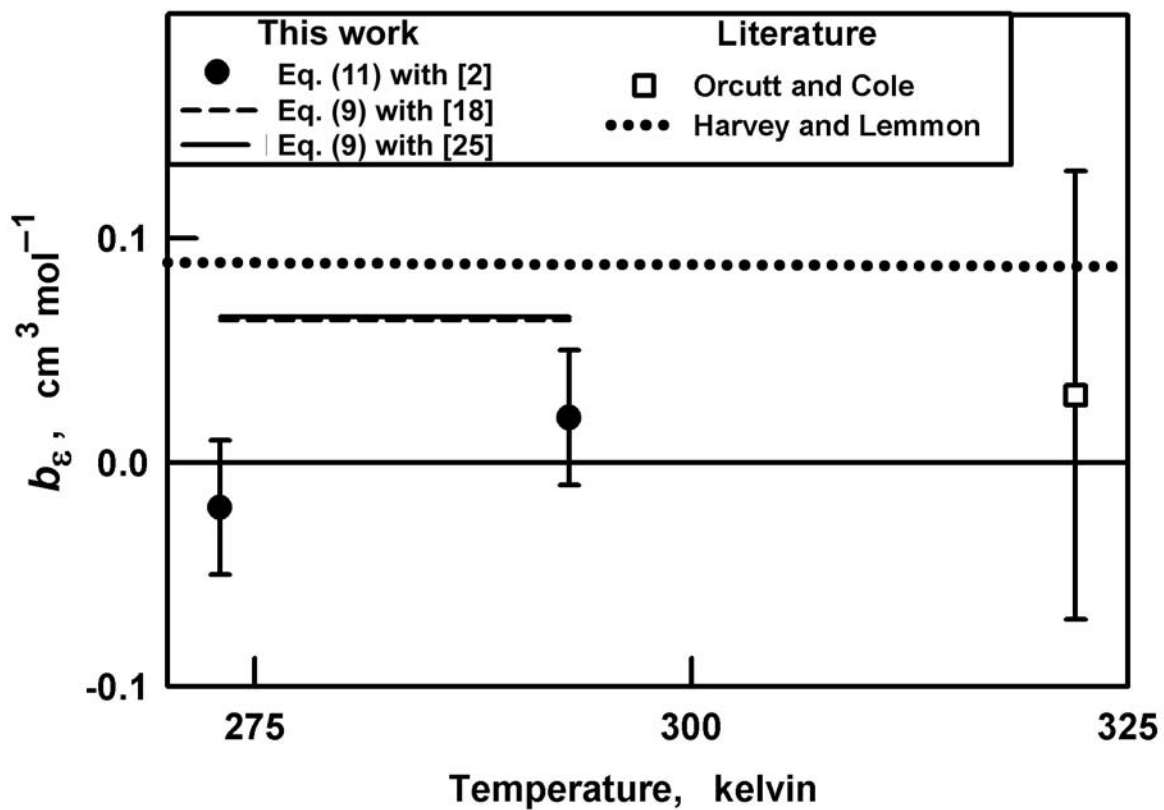


Figure 5. Estimates of the second dielectric virial coefficient of normal hydrogen.



REFERENCES

1. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London 1932).
2. K Patkowski, W. Ceneck, P. Jankowski, K. Szalewicz, J.B. Mehl, G. Garberoglio and A.H. Harvey, *J. Chem. Phys.* **129**, 094304 (2008).
3. J.B. Mehl, M.L. Huber, and A.H. Harvey, To be submitted to *Int. J. Thermophys* (2009).
4. H. Koch, C. Hattig, H. Larsen, J. Olsen, P. Jorgensen, B. Fernandez and A. Rizzo, *J. Chem. Phys.* **111**, 10099 (1999); A. Rizzo, C. Hattig, B. Fernandez, H. Koch, *J. Chem. Phys.* **117**, 2609 (2002).
5. D. F. Heller and W. M. Gelbart, *Chem. Phys. Lett.* **27**, 359 (1974).
6. J.L. Cacheiro, B. Fernando, A. Rizzo, B. Jansik and T.B. Pedersen, *Mol. Phys.* **106**, 881 (2008).
7. E. F. May, M.R. Moldover and J.W. Schmidt, *Phys. Rev. A* **78**, 032522 (2008).
8. J. W. Schmidt and M. R. Moldover, *Int. J. Thermophys.* **24**, 375 (2003).
9. E. F. May, L. Pitre, J. B. Mehl, M. R. Moldover and J. W. Schmidt, *Rev. Sci. Instrum.* **75**, 3307 (2004).
10. J. W. Schmidt, R. Gavioso, E. F. May and M. R. Moldover, *Phys. Rev. Lett.* **98**, 254504 (2007).
11. J. Rychlewski, *Mol. Phys.* **41** 833 (1980).
12. A.A. Maryott and F. Buckley, *Tables of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State* (National Bureau of Standards Circular 537, Washington 1953).
13. A. H. Harvey, private communication, 18 July 2008
14. A.H. Harvey and E. W. Lemmon, *Int. J. Thermophys.* **26**, 31 (2005).
15. J.W. Stewart, *J. Chem. Phys.* **40**, 3297 (1967)
16. A. Michels, P. Sanders and A. Schipper, *Physica* **2**, 753 (1935).
17. N.F. Ramsey, *Molecular Beams*, (Oxford University Press, New York, 1956.)
18. J. Rychlewski and W.T. Raynes, *Mol. Phys.* **41**, 843 (1980).

-
19. J.W. Leachman, R.T. Jacobsen, S.G. Penoncello, and E.W. Lemmon, "Fundamental Equations of State for Parahydrogen, Normal Hydrogen, and Orthohydrogen," Submitted to *J. Phys. Chem. Ref. Data* (2009).
 20. E. W. Lemmon, M. O. McLinden and M. L. Huber, *Reference Fluid Thermodynamic and Transport Properties*, NIST Standard Reference Database 23, Version 8.0 (Nat. Inst. Stands. Technol., Gaithersburg, Maryland, 2007).
 21. J.J. Hurly and J.B. Mehl, *J. Res. NIST* **112**, 75 (2007).
 22. G. Garberoglio and A.H. Harvey, "First-Principles Calculation of the Third Virial Coefficient of Helium," *J. Res. NIST.*, In preparation.
 23. A.L. Blancett, K.R. Hall and F.B. Canfield, *Physica* **47**, 75 (1970).
 24. G. Lach, J. Bogumil and K. Szalewicz, *Phys. Rev. Lett.* **92**, 233001 (2004).
 25. A. Rizzo, private communication, 22 July 2008.
 26. O. Kunz, R. Klimeck, W. Wagner and M. Jaeschke, *The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures* (GERG Technical Monograph 15, Dusseldorf, 2007.)
 27. R.H. Orcutt and R.H. Cole, *J. Chem. Phys.* **46** 697 (1967).
 28. A.C. Newell and R.C. Baird, *J. App. Phys.* **36**, 3751 (1965).
 29. A. Rizzo, C. Hattig, B. Fernandez and H. Koch, *J. Chem. Phys.* **117**, 2609 (2002).
 30. E. F. May, R. F. Berg, and M. R. Moldover, *Int. J. Thermophys.* **28**, 1085 (2007).