Frequency-Dependent Polarizability of Helium Including Relativistic Effects with Nuclear Recoil Terms

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Frequency-dependent polarizability of helium including relativistic effects with nuclear recoil terms

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Future metrology standards will be partly based on physical quantities computed from first principles rather than measured. In particular, a new pressure standard can be established if the dynamic polarizability of helium can be determined from theory with an uncertainty smaller than 0.2 ppm. We present calculations of the frequency-dependent part of this quantity including relativistic effects with full account of leading nuclear recoil terms and using highly optimized explicitly correlated basis sets. A particular emphasis is put on uncertainty estimates. At the He-Ne laser wavelength of 632.9908 nm, the computed polarizability value of 1.391 811 41 a.u. has uncertainty of 0.1 ppm that is two orders of magnitude smaller than those of the most accurate polarizability measurements. We also obtained an accurate expansion of the helium refractive index in powers of density.

Some physical quantities, for example, properties of the helium atom and interaction energies of helium atoms, can now be computed from first principles with precision rivaling and sometimes exceeding the best experimental determinations [1–3]. Therefore, quantities of this type can be used in establishing metrology standards. One example is a possible standard of temperature based on acoustic gas thermometry [4]. Another example is a pressure standard based on optical interferometry [5]. The current pressure standard dating back more than 300 years is realized by mercury manometers and can not be further improved. Also, the reference manometers are far from portable: 3 m high and containing 250 kg of mercury, a substance banned due to its toxicity. Since pressure is one of the most widely measured properties, in applications ranging from manufacturing of semiconductor chips to air-traffic control, a new pressure standard would significantly impact both technology and everyday life. The proposed standard [5] obtains pressure from the formula [6]

$$p = \frac{n^2-1}{n^2+2}\,\frac{3kT}{4\pi(\alpha+\chi)} + \cdots, \tag{1}$$

where n denotes the index of refraction of helium gas, k the Boltzmann constant, T the temperature, α the dipole polarizability, and χ the diamagnetic susceptibility of helium. To account for nonideality of helium gas, one has to include some small terms on the right-hand side depending on dielectric and density virial coefficients [6]. The essential part of the new standard is the determination of n with an uncertainty of 0.2 ppm via interferometric measurements of a variable-length cavity filled with helium and comparing to measurements in vacuum. The product kT, currently known with an uncertainty of 0.9 ppm [7] near the temperature of the triple point of water, is the subject of active research and a reduction of this uncertainty can be expected in near future. Since χ is five orders of magnitude smaller than α, it can be computed using the non-relativistic wave function from the expression $\chi = -e^2\langle r^2\rangle/3m_{\rm e}c^2$, where e and $m_{\rm e}$ are the electron charge and mass, c is the speed of light, and $\langle r^2\rangle$ is the average square of the electron-nucleus distance. Also the virial coefficients are known accurately enough from theory [3, 8]. However, α cannot currently be measured with uncertainty lower than 0.2 ppm, so the standard clings upon theory being able to achieve such accuracy. This Letter describes calculations of α from first principles. The resulting value of n can also be used to calibrate refractometers or to correct errors in interferometric length measurements [9].

Since the radiation frequency of interest, 632.9908 nm [10], is much smaller than the lowest resonance, the frequency dependence of α can be efficiently calculated from the power series expansion, $\alpha(\omega) = \alpha_0 + \alpha_2\,\omega^2 + \alpha_4\,\omega^4 + \cdots$, where α_0 is the static dipole polarizability. The coefficients α_k, $k > 0$, describing the frequency dependence of polarizability, will be referred to as the (polarizability) dispersion coefficients. We shall use the atomic units throughout (we never use reduced atomic units), a_0^3, where a_0 is the bohr radius $\hbar^2/m_e e^2$, as the unit of polarizability and the inverse of the atomic unit of time, $t_0 = \hbar^3/m_e e^4$, as the unit of frequency. For light systems like helium, each α_k can be expanded in powers of the fine structure constant $1/c$, where c=137.0359991 [7] is the speed of light expressed in atomic units, $\alpha_k = \alpha_k^{(0)} + \alpha_k^{(2)} + \alpha_k^{(3)} + \cdots$, $\alpha_k^{(l)}$ being proportional to $1/c^l$. We shall refer to $\alpha_k^{(2)}$ as the relativistic contributions. The terms $\alpha_k^{(3)}$, $\alpha_k^{(4)}$, etc., are due to radiative as well as higher-order relativistic effects predicted by quantum electrodynamics (QED).

The nuclear mass dependence of the nonrelativistic polarizability $\alpha_n^{(0)}$, can be taken into account exactly, but for the relativistic and QED contributions one has to use an expansion in powers of the ratio of $m_{\rm e}$ to the nuclear mass m_α, i.e., in powers of $1/M = m_{\rm e}/m_\alpha =$

1/7294.2995361. This subject has not been discussed in literature and we had to derive expression defining these effects. Since $1/M$ is of the order of 10^{-4}, keeping the linear term is entirely sufficient and such contributions can be represented in the form $\alpha_k^{(l)} = \alpha_k^{(l0)} + \alpha_k^{(l1)},\ l \geq 2$, where $\alpha_k^{(l0)}$ are computed with the infinite nuclear mass and $\alpha_k^{(l1)}$ are corrections of the order of $1/(Mc^l)$, referred to as the recoil corrections. These recoil corrections are expected to be negligible except for the static ones $\alpha_0^{(21)}$ and $\alpha_0^{(31)}$ and, possibly, for $\alpha_2^{(21)}$.

For comparisons with experiments, it is convenient to convert frequency to wave length $\lambda = 2\pi ce^2/\hbar\omega$

$$\alpha(\lambda) = A_0 + A_2\,\lambda^{-2} + A_4\,\lambda^{-4} + \cdots . \tag{2}$$

When $\alpha(\lambda)$ remains in atomic units and λ is measured in nm, then $A_k = f^k \alpha_k$, where $f = 2\pi c\, a_0/\text{nm} = 45.56335253$ (with a_0=0.05291772109 nm).

The static components of α obtained in the present work are consistent with the values of Ref. 1 to all digits shown in this reference, except for the term describing the electric-field dependence of the Bethe logarithm and for $\alpha_0^{(40)}$. We recomputed the former term using a different method than used in Ref. 1 obtaining a result that differs only marginally, by 0.011 $\mu a_0^3 \equiv 10^{-6} a_0^3$, the current value being more accurate. The term $\alpha_0^{(40)}$ was estimated in Ref. 1 by the contribution from the simple one-loop expression [11] and the uncertainty of this term was assumed to be 40%. Later, it was shown in Ref. 12 that the error of the one-loop approximation applied to the excitation energies of helium is only about 5%. Therefore, we reduced our error estimate from 40% to 25% or 0.14 μa_0^3, which we believe is still very conservative.

The dispersion coefficients α_k (k = 2, 4, 6) were calculated thus far only by Bhatia and Drachman (BD) [13, 14]. These authors did not provide any estimates of the uncertainties. Their relativistic contributions do depend on the nuclear mass but the recoil effect, $\alpha_k^{(21)}$, was not correctly taken into account, vide infra. Furthermore, the A_k coefficients were incorrectly converted from the reduced Rydberg units: the factor $(1 + m_e/m_\alpha)^k$, appearing in the conversion formula, was erroneously replaced by its square $(1 + m_e/m_\alpha)^{2k}$.

At the nonrelativistic level of theory, $\alpha(\omega)$ of an atom in a quantum state ψ is defined by the standard polarization propagator expression

$$\alpha(\omega) = \langle\psi|z\,\mathcal{R}(\omega)z|\psi\rangle + \langle\psi|z\,\mathcal{R}(-\omega)z|\psi\rangle, \tag{3}$$

where $z = z_1 + z_2$, with z_i denoting electron coordinates, and $\mathcal{R}(\omega) = Q\,(QH - E + \omega)^{-1}$ is the resolvent of the atomic Hamiltonian H, with $Q = 1 - P = 1 - |\psi\rangle\langle\psi|$ and E being the energy of state ψ. For the helium atom

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}(\nabla_1 + \nabla_2)^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}. \tag{4}$$

$\mathcal{R}(\omega)$ satisfies the identity $\mathcal{R}(\omega) = \mathcal{R} - \omega\,\mathcal{R}\,\mathcal{R}(\omega)$, where $\mathcal{R} = Q\,(QH - E)^{-1}$ is the static (reduced) resolvent of H. Iterating this expression and inserting it into Eq. (3), one obtains

$$\alpha_k^{(0)} = 2\,\langle\psi|z\,\mathcal{R}^{k+1}z|\psi\rangle. \tag{5}$$

To account for the leading relativistic contributions of the order of $1/c^2$ assuming infinite nuclear mass, we add to the Hamiltonian of Eq. (4) the perturbation from the Breit-Pauli Hamiltonian [15] obtaining

$$\alpha_0^{(20)} = -4\,\langle\psi_0|B_1\mathcal{R}_0z\mathcal{R}_0z\psi_0\rangle - 2\,\langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0z\psi_0\rangle,$$

$$\begin{aligned}\alpha_2^{(20)} = &-4\,\langle\psi_0|B_1\mathcal{R}_0z\mathcal{R}_0^3z\psi_0\rangle - 4\,\langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0^3z\psi_0\rangle\\ &-2\,\langle\psi_0|z\mathcal{R}_0^2\overline{B}_1\mathcal{R}_0^2z\psi_0\rangle,\end{aligned}$$

$$\begin{aligned}\alpha_4^{(20)} = &-4\,\langle\psi_0|B_1\mathcal{R}_0z\mathcal{R}_0^5z\psi_0\rangle - 4\,\langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0^5z\psi_0\rangle\\ &-4\,\langle\psi_0|z\mathcal{R}_0^2\overline{B}_1\mathcal{R}_0^4z\psi_0\rangle - 2\,\langle\psi_0|z\mathcal{R}_0^3\overline{B}_1\mathcal{R}_0^3z\psi_0\rangle,\end{aligned}$$

$$\begin{aligned}\alpha_6^{(20)} = &-4\,\langle\psi_0|B_1\mathcal{R}_0z\mathcal{R}_0^7z\psi_0\rangle - 4\,\langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0^7z\psi_0\rangle\\ &-4\,\langle\psi_0|z\mathcal{R}_0^2\overline{B}_1\mathcal{R}_0^6z\psi_0\rangle - 4\,\langle\psi_0|z\mathcal{R}_0^3\overline{B}_1\mathcal{R}_0^5z\psi_0\rangle\\ &-2\,\langle\psi_0|z\mathcal{R}_0^4\overline{B}_1\mathcal{R}_0^4z\psi_0\rangle,\end{aligned}$$

where

$$\begin{aligned}B_1 = &-\frac{1}{8c^2}(\nabla_1^4 + \nabla_2^4) + \frac{\pi}{c^2}[\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)] + \frac{\pi}{c^2}\delta(\boldsymbol{r}_{12})\\ &+\frac{1}{2c^2}[\nabla_1 r_{12}^{-1}\nabla_2 + (\nabla_1\boldsymbol{r}_{12})r_{12}^{-3}(\boldsymbol{r}_{12}\nabla_2)],\end{aligned} \tag{6}$$

$\overline{B}_1 = B_1 - \langle\psi_0|B_1\psi_0\rangle$, and the quantities with subscript 0 are analogous to those defined above but for infinite-mass nonrelativistic Hamiltonian.

The relativistic recoil term $\alpha_0^{(21)}$ is equal $\alpha_0^{(21)}(B_2) + \alpha_0^{(21)}(H_1B_1)$, where $H_1 = -\frac{1}{2M}(\nabla_1 + \nabla_2)^2$ and

$$\begin{aligned}B_2 = \frac{1}{Mc^2}\Big[&\nabla_1 r_1^{-1}\nabla_1 + (\nabla_1\boldsymbol{r}_1)r_1^{-3}(\boldsymbol{r}_1\nabla_1) + \nabla_1 r_1^{-1}\nabla_2\\ &+ (\nabla_1\boldsymbol{r}_1)r_1^{-3}(\boldsymbol{r}_1\nabla_2) + \nabla_2 r_2^{-1}\nabla_1 + (\nabla_2\boldsymbol{r}_2)r_2^{-3}(\boldsymbol{r}_2\nabla_1)\\ &+ \nabla_2 r_2^{-1}\nabla_2 + (\nabla_2\boldsymbol{r}_2)r_2^{-3}(\boldsymbol{r}_2\nabla_2)\Big].\end{aligned} \tag{7}$$

The two components are given by

$$\alpha_0^{(21)}(B_2) = -4\,\langle\psi_0|B_2\mathcal{R}_0z\mathcal{R}_0z\psi_0\rangle - 2\,\langle\psi_0|z\mathcal{R}_0\overline{B}_2\mathcal{R}_0z\psi_0\rangle \tag{8}$$

where $\overline{B}_2$ is defined in the same way as $\overline{B}_1$ and

$$\begin{aligned}&\alpha_0^{(21)}(H_1B_1) =\\ &\quad 4\,\big[\langle\psi_0|z\mathcal{R}_0z\mathcal{R}_0\overline{H}_1\mathcal{R}_0B_1\psi_0\rangle + \langle\psi_0|z\mathcal{R}_0z\mathcal{R}_0\overline{B}_1\mathcal{R}_0H_1\psi_0\rangle\\ &\quad + \langle\psi_0|z\mathcal{R}_0\overline{H}_1\mathcal{R}_0z\mathcal{R}_0B_1\psi_0\rangle + \langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0z\mathcal{R}_0H_1\psi_0\rangle\\ &\quad + \langle\psi_0|z\mathcal{R}_0\overline{H}_1\mathcal{R}_0\overline{B}_1\mathcal{R}_0z\psi_0\rangle + \langle\psi_0|H_1\mathcal{R}_0z\mathcal{R}_0z\mathcal{R}_0B_1\psi_0\rangle\\ &\quad - \langle\psi_0|z\mathcal{R}_0z\psi_0\rangle\langle\psi_0|H_1\mathcal{R}_0^2B_1\psi_0\rangle\\ &\quad -\langle\psi_0|z\mathcal{R}_0^2z\psi_0\rangle\langle\psi_0|H_1\mathcal{R}_0B_1\psi_0\rangle\big],\end{aligned} \tag{9}$$

where $\overline{H}_1 = H_1 - \langle\psi_0|H_1\psi_0\rangle$.

The correction $\alpha_2^{(21)}$ is very small and can be computed using a finite difference expression

$$\alpha_2^{(21)} \approx \alpha_2^{(20)}(B_1 \to B_2) + \alpha_2^{(20)}(H_0 \to H) - \alpha_2^{(20)}, \quad (10)$$

valid to the order of $1/(M^2c^2)$, where $B_1 \to B_2$ means that operator B_1 in the expression for $\alpha_2^{(20)}$ should be replaced by B_2 and similarly $H_0 \to H$ means that quantities computed with the Hamiltonian H_0 should be replaced by those computed with H.

To evaluate $\alpha_k^{(li)}$, accurate representations of the helium ground-state wave functions ψ_0 and ψ were obtained by minimizing the Rayleigh-Ritz functional for the Hamiltonians H_0 and H, respectively. We also need four auxiliary functions, which were obtained recursively from Hylleraas-type functionals

$$J_0^{(n)}[\tilde{\phi}] = \langle\tilde{\phi}|H_0 - E_0 + P_0|\tilde{\phi}\rangle - 2\langle\tilde{\phi}|\phi_0^{(n-1)}\rangle \quad (11)$$

for $\phi_0^{(n)} = \mathcal{R}_0^n z\psi_0$ and

$$K_0^{(n)}[\tilde{\psi}] = \langle\tilde{\psi}|H_0 - E_0 + P_0|\tilde{\psi}\rangle - 2\langle\tilde{\psi}|(1-P_0)z\phi_0^{(n)}\rangle\,, \quad (12)$$

for $\psi_0^{(n)} = \mathcal{R}_0 z\phi_0^{(n)}$, and analogous functionals obtained by dropping all the subscripts 0 for $\phi^{(n)} = \mathcal{R}^n z\psi$ and $\psi^{(n)} = \mathcal{R}z\phi^{(n)}$. The trial functions used in all minimization processes were expanded in bases of Slater geminals

$$\tilde{\phi} = (1 + \mathcal{P}_{12})\, Y(\mathbf{r}_1, \mathbf{r}_2) \sum_{i=1}^{N} c_i \mathrm{e}^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}}\,, \quad (13)$$

where $\mathcal{P}_{12}$ is the transposition operator whereas $Y(\mathbf{r}_1, \mathbf{r}_2) = z_1$ in calculations of $\phi_0^{(n)}$ and $\phi^{(n)}$ and $Y(\mathbf{r}_1, \mathbf{r}_2) = 1$ otherwise. One may note that the functions $\psi_0^{(n)}$ and $\psi^{(n)}$ contain also a D-wave component, but it does not contribute to matrix elements that are needed. The linear coefficients were obtained by solving the appropriate set of linear equations, while to determine the nonlinear parameters we employed two strategies: the full optimization (FO) and the stochastic optimization (SO). In the latter case, the parameters α_i, β_i, γ_i are pseudo-randomly generated from a box with optimized dimensions. We used two boxes to model the short-range and medium-range asymptotics of the wave functions. To eliminate possibilities of numerical errors, the FO and SO based codes (including the integral and linear algebra routines) were programmed entirely independently by different members of our team.

The contributions $\alpha_k^{(0)}$ for $k = 0, 2, 4, 6$ were computed for several values of N, up to 600 (800) in the FO (SO) approach, both optimizations giving at least 11 convergent digits, with FO converging faster. Our results agree to 9, 8, 4, and 7 digits, respectively, with the values obtained by BD [13]. Using the SO procedure, we also calculated: $\alpha_8^{(0)}$=4.39500532(1), $\alpha_{10}^{(0)}$=6.7725956(1), $\alpha_{12}^{(0)}$=10.622083(1), and $\alpha_{14}^{(0)}$=16.86118(1) a.u.

For the relativistic contributions $\alpha_k^{(20)}$, $k = 0, 2, 4, 6$, the convergence is much slower than in the nonrelativistic case. This is due to the fact that we use nonrelativistic functionals which are sensitive to wave function values in different regions of the configuration space than the relativistic operators (these operators are too singular to be used in optimizations). The SO procedure leads now to a faster convergence than FO since randomly chosen exponents cover the space more uniformly than FO exponents. Thus, we used the SO results as our recommended values and in estimates of uncertainty. Nevertheless, the agreement to 6, 5, 3, and 3 digits, respectively, between the two sets of results is more than sufficient for the present purposes. Our values are substantially more accurate than those of BD [14], with agreement to only 2, 2, and 1 digit, respectively (BD did not compute $\alpha_6^{(20)}$). For $\alpha_0^{(20)}$, our value is consistent with, but significantly more accurate than the results of Refs. [1, 16, 17]. The relativistic recoil contribution $\alpha_0^{(21)}$ is $-0.0935(1)$ μa_0^3. Its smallness results from some cancellation of its components, $\alpha_0^{(21)}(H_1B_1)$ and $\alpha_0^{(21)}(B_2)$, equal to 0.1559 and -0.2494 μa_0^3, respectively. The contribution $\alpha_2^{(21)}$ is equal to $-0.144(1)$ $\mu a_0^3\, t_0^2$, so it is virtually negligible.

It should be pointed out that the relativistic contributions computed by BD [14] depend on the nuclear mass and, strictly speaking, should not be compared with our, nuclear-mass-independent contributions $\alpha_k^{(20)}$. This is because these authors incorrectly assumed that the individual terms in the Breit-Pauli Hamiltonian are proportional to (inverse) powers of the reduced electron mass rather than the real mass. Therefore, although the nuclear-mass-dependent part of their relativistic contributions is of the order of $1/(Mc^2)$, it differs from the $\alpha_k^{(21)}(B_1H_1)$ part of the true recoil correction. Additionally, BD completely neglected the contribution $\alpha_k^{(21)}(B_2)$. Thus, their relativistic contributions cannot be viewed as approximations to $\alpha_k^{(20)} + \alpha_k^{(21)}$. Since the effects of the order of $1/(Mc^2)$ are very small, the differences between our relativistic contributions and those of BD are mainly due to the differences in basis sets used in the calculations rather than to the treatments of the nuclear mass dependence.

After correcting the units conversion error in Ref. 14, the A_k coefficients computed by BD agree with our values to 5, 6, 4, and 5 digits for $k = 0, 2, 4, 6$, respectively. For $k = 0$, the discrepancy is mainly due to the $1/c^3$ terms not considered by BD. The reasons for the low accuracy of A_4 are unclear. Due to the smallness of the relativistic contributions to A_k, the overall agreement is good despite the fact that the relativistic contributions from BD work are significantly less accurate than ours.

In Table I, we present the dynamic polarizability of

TABLE I. Dynamic polarizability of ^{4}He [a_0^3] at $\lambda = 632.9908$ nm.

static	nonrelativistic	1.383 809 98641(1)
	$1/c^2$ [a]	−0.000 080 4534(1)
	$1/c^3$ [b]	0.000 030 655(1)
	$1/c^4$	0.000 000 56(14)
	finite nuclear size[c]	0.000 000 0217(1)
	total	1.383 760 77(14)
λ^{-2}	nonrelativistic	0.007 995 7979(1)
	relativistic[d]	−0.000 000 1721(1)
	total	0.007 995 6258(1)
λ^{-4}	nonrelativistic	0.000 054 8363(1)
	relativistic	0.000 000 00014(1)
	total	0.000 054 8364(1)
λ^{-6}	nonrelativistic	0.000 000 4076(1)
	relativistic	0.000 000 0000(1)
	total	0.000 000 4076(1)
λ^{-8}	nonrelativistic	0.000 000 0032(1)
$\alpha(\lambda) - \alpha(0)$	present[e]	0.008 050 8730(1)
	BD[f]	0.008 050 871
total	present	1.391 811 64(14)
	BD[g]	1.391 780 800

[a] Includes the recoil correction of the order of $1/(Mc^2)$ equal to $-0.000\,000\,0935(1)$. [b] From Ref. 1 except for the contribution from the electric field derivative of the Bethe logarithm equal to 0.000 000 182(1) [18]. [c] Computed adding the correction term $(4/3)\pi\, r_\alpha^2\, [\,\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)\,]$ to H, where $r_\alpha = 1.676$ fm is the nuclear charge radius of ^{4}He. [d] Including the recoil correction of the order of $1/(Mc^2)$ equal to $-0.000\,000\,00075(1)$. [e] The contribution of the λ^{-10} term, amounting to 2.5×10^{-11}, is negligible. [f] Calculated using correctly converted A_k constants. Equation (15) of Ref. 14 gives 0.008 052 951, i.e., 0.03% error resulting in 1.7 ppm error in the total value of $\alpha(632.9908)$. [g] Using the static value of BD equal to 1.383 729 929.

^{4}He. In addition to the contributions discussed earlier, we included the effect of finite nuclear size which is almost negligible. The dispersion part of $\alpha(632.9908)$, i.e., the contribution explicitly dependent on wavelength, agrees to 6 significant digits with the result of BD (after conversion errors are corrected) due to the high, eight-digit accuracy of BD's $\alpha_2^{(0)}$ contribution. However, the total polarizability obtained by us differs significantly from BD's result: only 5 digits agree and the discrepancy is about 22 ppm. As already discussed, this difference is mainly due to the QED effects neglected by these authors. The second source of the difference is our significantly improved value of the static relativistic component. The uncertainty of our recommended value of $\alpha(632.9908)$ amounts 0.14 μa_0^3, i.e., about 0.1 ppm. This accuracy is sufficient for the purpose of the new pressure standard but one should ask if any neglected effects could contribute above the uncertainty estimate. The potential candidates are the QED recoil correction $\alpha_0^{(31)}$ of the order of $1/(Mc^3)$, the QED contribution to the polarizability dispersion $\alpha_2^{(30)}$ of the order of $1/c^3$ and, finally, and probably most importantly, the remaining, other than one-loop contributions to $\alpha_0^{(40)}$ of the order of $1/c^4$. We conservatively estimated the possible magnitudes of the neglected contributions and found that their sum should be below 0.1 ppm. This uncertainty is already included in the final error bar given in Table I.

TABLE II. Virial expansion of refractive index. $a_r = \frac{2}{3}a_n$, b_n, and c_n are in units of cm^3/mol, cm^6/mol^2, and cm^9/mol^3, respectively, and λ is in nm. 1 cm^3/mol = 11.205 8721 a_0^3.

$a_r(0)$	present	0.517 246 21(6)[a,b]
	exp. [6]	0.517 245 5(47)
$a_r(632.9908)$	present	0.520 255 64(6)[c,d]
	exp. [19, 20]	0.521 3(1)
	exp. [21]	0.522 0(3)
$a_r(546.2268)$	present	0.521 297 25(6)
	exp. [22]	0.521 57(15)[e]
$b_n(0)$	present, 273.16 K	0.0245(2)[f]
$b_n(632.9908)$	present, 273.16 K	0.0238(2)[f]
	present, 302 K	0.0184(2)[f]
	present, 323 K	0.0151(2)[f]
	exp. [20]	0.000(15)[g]
$c_n(0)$	present, 273.16 K	-0.93(25)[f]

[a] $a_n = 8.694\,292\,2(9)\ a_0^3$ or $0.775\,869\,31(8)(4)$ cm^3/mol, where the second uncertainty originates from the Avogadro constant $6.022\,141\,29(27)\times10^{23}$. [b] Computed using $\chi = -0.000\,021\,194(1)\ a_0^3$ [23], the uncertainty reflects the estimated size of relativistic contributions. [c] $a_n = 8.744\,8758(9)\,a_0^3 = 0.780\,383\,35(8)(4)$ cm^3/mol. [d] We neglected the frequency dependence of χ, a relativistic effect expected to be very small. [e] Inferred from measured value of $n-1 = 34.895(10)\times10^{-4}$ at T=273.16 K and p=101.325 kPa. [f] Computed using b_ε=−0.0978(2) cm^3/mol [24] (uncertainty estimated based on comparison with Ref. 8) and c_ε =−1.34(36) cm^6/mol^2 [6, 25], T=273.16 K. For other T: $b_\varepsilon(303) = -0.1065(2)$ cm^3/mol and $b_\varepsilon(323) = -0.1107(2)$ cm^3/mol [24]. [g] Computed from $a_r = 0.5213(1)$ cm^3/mol and $b_r = \frac{2}{3}b_n - \frac{1}{4}a_r = -0.068(10)$ cm^6/mol^2 measured in Ref. 20, same value obtained for both temperatures.

The virial expansion for the refractive index can be written as

$$n = 1 + a_n\rho + b_n\rho^2 + c_n\rho^3 + \cdots, \tag{14}$$

$$a_n = 2\pi(\alpha + \chi), \tag{15}$$

$$b_n = 2\pi(\alpha b_\varepsilon + \tfrac{1}{3}\pi\alpha^2 + \chi b_\mu + \tfrac{1}{3}\pi\chi^2 + 2\pi\alpha\chi), \tag{16}$$

$$c_n = 2\pi(\alpha c_\varepsilon + \tfrac{2}{3}\pi\alpha^2\, b_\varepsilon + \tfrac{10}{9}\pi^2\alpha^3), \tag{17}$$

where ρ is density, b_ε and c_ε are the dielectric virial coefficients and b_μ is the magnetic permeability virial coefficient. We have written down the term χb_μ in Eq. (16), but we will neglect it in numerical calculations since χ is about five orders of magnitude smaller than α and b_μ (unknown) is expected to be at the most of the same order as b_ε. We completely ignored the magnetic part of c_n in Eq. (17). After Eq. (14) is squared, it becomes consistent with Eq. (4) of Ref. 6 within the terms included there except that the factor of 2 is missing in front of the

$A_\varepsilon^2\, b\, \rho^2$ term. Equation (14) can be easily solved for ρ and the resulting formula can be used for a determination of density, or, when combined with the virial equation of state, also for a determination of pressure.

The virial coefficients are presented in Table II. The agreement with the measurement of Schmidt *et al.* [6] is excellent, to within 1.4±9.1 ppm. Note that the authors of Ref. 6 reported the value of a_r with a subtracted magnetic contribution $4\pi\chi/3 = -0.0000080$ cm^3/mol, which was added back in Table II. The agreement of theory with measurements at 632.9908 nm [19–21] is, however, poor, as noticed earlier by BD [14] and by Stone and Stejskal [9]. The disagreement with the measurement of Leonard [22] is smaller, only about twice the experimental uncertainty. The apparent better agreement of theory with this experiment (within 1σ) found in Ref. 14 was due to the neglect [14] of the nonlinear dependence of density on pressure. The values of b_n and c_n presented in Table II have uncertainties due entirely to uncertainties of b_ε and c_ε. The third and fourth term in Eq. (16) make negligible contributions and there is substantial cancellation between the first two terms. The experimental b_n determined from the values measured in Ref. [20] is consistent with zero, which is almost within the combined theoretical and experimental uncertainties. From our data and from the $b_\varepsilon(T)$ data of Ref. 24 we predict that b_n will vanish only around 415 K. Since b_n is small at T=273.16 K and higher temperatures, its accuracy is sufficient to predict $n-1$ with a 1 ppm uncertainty for pressures up to 10 MPa.

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