# The effect of intermolecular interactions on the electric properties of helium and argon. II. The dielectric, refractivity, Kerr, and hyperpolarizability second virial coefficients

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The dielectric, refractivity, Kerr, and hyperpolarizability second virial coefficients for the helium and argon gases are evaluated for a wide range of temperatures using a semiclassical approach and the high quality frequency-dependent interaction induced electric polarizabilities and second hyperpolarizabilities of the previous paper. For helium and argon we obtain satisfactory agreement with most of the experimental data for the dielectric and the refractivity second virial coefficients. Our results confirm that the helium gas second Kerr virial coefficient is very small at temperatures beyond 70 K. For argon we obtain a very good agreement with a recent experimental determination at 632.8 nm, whereas we suggest that previous experimental results for 458 nm might be inaccurate. The ESHG results indicate a possible disagreement between a recent experimental determination and the semiclassical ansatz for the second hyperpolarizability virial coefficients. © *1999 American Institute of Physics.* [S0021-9606(99)31046-1]

## I. INTRODUCTION

In a recent study,[1] which in the following is referred to as ''Part I,'' we calculated the frequency-dependent interaction induced polarizabilities and second hyperpolarizabilities for the $He_2$ and $Ar_2$ van der Waals complexes using the coupled cluster singles and doubles (CCSD) and, for $He_2$, also the full configuration interaction (FCI) method. A FCI potential energy curve for $He_2$ was obtained. Fernández and Koch[2] determined a CCSD including connected triples corrections (CCSD(T)) potential energy curve for the $Ar_2$ dimer. All the calculations were carried out with extended basis sets. We exploit here these accurate *ab initio* data to evaluate the dielectric, the refractivity, the Kerr, and the hyperpolarizability second virial coefficients of the helium and argon gases in a wide range of temperatures.

Much work has been carried out on the determination of these virial coefficients, both from an experimental and a theoretical point of view. However, the accuracy of the calculations for the virial coefficients has been hampered, in particular for argon, by the limited accuracy with which interaction induced changes of polarizabilities and hyperpolarizabilities could be computed and by the fact that the dispersion contribution to these frequency-dependent properties has not been considered.

A detailed review of previous investigations on the argon virial coefficients was given in Ref. 3, where the dielectric, refractivity, Kerr, and hyperpolarizability second virial coefficients were evaluated and reasonable agreement with experiment was obtained. A rather extensive analysis of the effects of basis set size, electron correlation, and frequency dependence of the properties suggested that the observables were especially sensitive to the basis set and that new calculations with more extended and diffuse basis sets would be needed to improve the agreement with experiment. The results of such calculations are reported in Part I, and the evaluation of the virial coefficients is discussed here.

The dielectric virial coefficient of helium has been determined both by direct[4–7] and indirect[8–11] methods at temperatures ranging from as low as 4.22 K up to 323.15 K. Data are also available at 3.799 K.[12] The low temperature data are highly scattered. The refractivity virial coefficients were measured at 303 and 323 K by Achtermann *et al.* using a differential-interferometric technique.[9,11] The comparison with theoretical values—based on a classical dipole-induced-dipole (DID) model—gave rather poor results, whereas a more refined semiclassical approach, using both a DID model and estimates taken from the *ab initio* results of Dacre[13] for the trace of the polarizability tensor, was shown to give much better agreement. Orcutt and Cole[5] also mea-

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sured the refractive coefficient of helium at 323 K.

Buckingham and Dunmur measured the Kerr electro-optic effect of rare gases at $\lambda = 632.8$ nm in 1967.[14] They determined the dependence of the Kerr constant on the density and found no deviations from a linear law for both helium and neon, whereas a quadratic behavior was evident for argon. Tammer *et al.*[15] studied the dc-Kerr effect of helium at 632.8 nm again some 25 years later. Their experiment, made at a temperature of 303.7 K and in a range of pressures between 76 and 97 bar, confirmed that virial coefficients of order higher than first (thus including $B_K$,) are so small that they could not be determined at ''(...) the present stage of experimental accuracy.''

Previous theoretical studies have shown that the determination of the virial coefficients for linear and nonlinear optical properties is a challenging task. Coupled Hartree–Fock results for the second dielectric virial coefficient of helium were obtained by Fortune *et al.*[16,17] Dacre has studied the second dielectric virial coefficients of both helium [at the SCF and correlated—configuration interaction singles and doubles (CISD)—levels][13] and argon (at the SCF level).[18] Hohm determined the frequency- and temperature-dependencies of the second refractivity virial coefficients for several atoms and small molecules.[19] He used a DID based theoretical model and observed significant deviations with respect to the available experimental results. Hohm *et al.*[20] studied also in detail the temperature dependence of the second dielectric virial coefficients of rare gases, and found that it could not be reproduced with then existing theories.

In their experimental study of the hyperpolarizabilities of interacting molecular pairs, Donley and Shelton estimated the second virial coefficients of the ESHG hyperpolarizability ratios using a Lennard-Jones 6-12 potential and the DID model. The procedure was not sufficiently adequate to provide good accuracy of the properties.[21,22]

Using quantum statistical mechanics, Bruch *et al.* derived the second dielectric and upper and lower bounds to the second Kerr virial coefficients for helium.[23] For the former, at 4 K, they obtained an agreement with respect to experiment only on the order of magnitude. This reflects a lack of precision in the estimated interaction polarizability.

The second dielectric and the second hyperpolarizability virial coefficients of helium were evaluated by Bishop and Dupuis from fourth-order Møller–Plesset perturbation theory (MP4).[24] For the former, good agreement was obtained with the experimental data and with a previous theoretical CISD result. No experimental data are available for the latter.

Moszynski *et al.* used symmetry-adapted perturbation theory (SAPT) (Refs. 25, 26) results for the potential curve and for the interaction property to compute the dielectric second virial coefficient of helium.[27–29] First and second quantum corrections to the semiclassical results were calculated.[28] A considerable discrepancy was then found with respect to experiment at low temperatures, where the semiclassical expansion is divergent. Full quantum-statistical calculations[27] allow to correct these discrepancies, and the divergence vanishes. The quality of the results allowed the authors to get some understanding of the scattering of experimental data at low temperatures, and to suggest new experimental measurements.

In the next section, we summarize the formulas used to evaluate the virial coefficients semiclassically. In Sec. III we briefly describe the computational approach. The results are given and discussed in Sec. IV. The last section contains some concluding remarks.

## II. THEORY

In Part I we have discussed the evaluation of the frequency-dependent interaction induced polarizabilities and hyperpolarizabilities.[3] Here we only summarize the relations between these properties and the different virial coefficients. As in Part I, we denote the interaction induced electric dipole average polarizability, polarizability anisotropy, second dc-Kerr hyperpolarizability, and isotropic parallel second hyperpolarizability with $\Delta\alpha_{\rm ave}(\omega,R)$, $\Delta\alpha_{\rm ani}(\omega,R)$, $\Delta\gamma_K(\omega,R)$, and $\Delta\gamma_{\parallel}(\omega_0,\omega_1,\omega_2,\omega_3,R)$, respectively. All *ab initio* data for the interaction induced properties are counterpoise corrected results and their frequency dependence is described through dispersion relationships involving the static values and the Cauchy moments $\Delta S(-4)$ or the hyperpolarizability dispersion coefficients $A$, see Part I.

The second dielectric and the second refractivity virial coefficients are obtained from the expansion of the generalization of the Clausius–Mossotti function in orders of the molar density $\rho$ (the inverse molar volume) of the gas.[30] For temperatures $T$ for which the thermal energy $kT$—with $k$ indicating the Boltzmann constant—is large compared to the dissociation energy of the van der Waals dimer the second refractivity virial coefficient can be calculated from the classical statistical mechanics expression,[31]

$$\begin{aligned} B_R(\omega,T) &= \frac{N_A^2}{6\epsilon_0} X_{\alpha_{\rm ave}}(\omega,T) \\ &= \frac{N_A^2}{6\epsilon_0} 4\pi \int_0^\infty \Delta\alpha_{\rm ave}(\omega,R) \\ &\quad \times \exp(-V(R)/kT) R^2 dR, \end{aligned} \tag{1}$$

where $V(R)$ is the interatomic potential. $N_A$ is Avogadro's number, and $\epsilon_0$ the vacuum permittivity. For very low temperatures, quantum corrections, which account for the discrete rovibrational levels of the van der Waals molecule, must be included, see, for instance, Refs. 27–29. Here we assume that the classical approximation can be used. Thus we restrict our study to the determination of the zeroth-order expansion in powers of $\hbar$[23,28,32] as given by the semiclassical expression in Eq. (1). We approximate the frequency dependence of the refractivity virial coefficient by expanding it in a power series in $\omega$ up to second order,

$$B_R(\omega,T) = B_R^{(0)}(T) + \omega^2 B_R^{(2)}(T) + \cdots, \tag{2}$$

where the static limit $B_R^{(0)}(T)$ is identical to the second dielectric virial coefficient $B_\epsilon(T)$.[33] The coefficients $B_R^{(0)}(T)$ and $B_R^{(2)}(T)$ are calculated analogous to $B_R(\omega,T)$, Eq. (1), but with $\Delta\alpha_{\rm ave}(\omega,R)$ replaced by the interaction-induced static polarizability and the Cauchy moment, $\Delta\alpha_{\rm ave}(0,R)$ and $\Delta S_{\rm ave}(-4,R)$, respectively.

The interaction-induced polarizability anisotropy $\Delta\alpha_{\rm ani}(\omega,R)$ is related to the pressure-dependence of the dc-Kerr or electro-optical effect.[34] The latter is conveniently expressed by an expansion of the molar Kerr constant ${}_mK$ as a power series in the density.[14] The second Kerr virial coefficient $B_K(\omega,T)$ can be calculated as[33,14]

$$B_K(\omega,T)=\frac{N_A^2}{162\epsilon_0}\left(\frac{1}{5kT}X_K^{\alpha}(\omega,T)+X_K^{\gamma}(\omega,T)\right)$$
$$=B_K^{\alpha}(\omega,T)+B_K^{\gamma}(\omega,T), \tag{3}$$

with the integrals $X_K^{\alpha}(\omega,T)$ and $X_K^{\gamma}(\omega,T)$ given by

$$X_K^{\alpha}(\omega,T)=4\pi\int_0^{\infty}\Delta\alpha_{\rm ani}(\omega,R)\Delta\alpha_{\rm ani}(0,R)$$
$$\times\exp(-V(R)/kT)R^2dR, \tag{4}$$

$$X_K^{\gamma}(\omega,T)=4\pi\int_0^{\infty}\Delta\gamma_K(\omega,R)\exp(-V(R)/kT)R^2dR. \tag{5}$$

Bruch *et al.*[23] have determined an expression for the upper and lower bounds to the classical expression, Eq. (4), within a quantum statistical approach, and they have discussed the implications in the calculation of the second Kerr virial coefficient of helium at very low temperatures.

Since in particular the dispersion contribution to $B_K^{\gamma}(\omega,T)$ makes only a small correction to the dominant contribution $B_K^{\alpha}(\omega,T)$, we have assumed here—as in Ref. 3—that Kleinman symmetry[35] is valid in the calculation of $X_K^{\gamma}(\omega,T)$ (see Sec. III). Thus $5\gamma_{\parallel}=\gamma_{zzzz}+4\gamma_{xxzz}+8\gamma_{xxyy}$ and $\Delta\gamma_K(\omega,R)\approx\Delta\gamma_{\parallel}(-\omega,0,0,\omega,R)$. Kleinman symmetry is exact in the static limit, and a (often very good) approximation for the frequency-dependent part. Again we expand $X_K^{\alpha}(\omega,T)$ and $X_K^{\gamma}(\omega,T)$ as power series in $\omega$ up to second order using the corresponding expansion of the properties $\Delta\alpha_{\rm ani}(\omega,R)$ and $\Delta\gamma_K(\omega,R)$.

Following the general treatment by Buckingham and Pople,[33] in Ref. 3 a virial expansion for the second hyperpolarizability was introduced,

$$\gamma(\Omega,\rho,T)=\gamma(\Omega)+B_{\gamma}(\Omega,T)\rho+\cdots, \tag{6}$$

where $\Omega$ is a shorthand notation for the usual sequence of frequency arguments $\omega_0$, $\omega_1$, $\omega_2$, and $\omega_3$. Within the semiclassical approximation the coefficient $B_{\gamma}(\Omega,T)$ is given by

$$B_{\gamma}(\Omega,T)=\frac{N_A}{8\pi\epsilon_0}X_{\gamma}(\Omega,T), \tag{7}$$

with

$$X_{\gamma}(\Omega,T)=4\pi\int_0^{\infty}\Delta\gamma_{\parallel}(\Omega,R)\exp(-V(R)/kT)R^2dR. \tag{8}$$

In ESHG experiments the hyperpolarizability of a gas, and thus its pressure-dependence, can only be measured relative to that of a second reference gas. Thus, for comparison with experiment we report in the tables and figures of Sec. IV C the quantity $b_A(\Omega,T)=B_{\gamma,A}(\Omega,T)/\gamma_A(\Omega)$, where the subscript ''*A*'' identifies the system. As for the interaction-induced polarizabilities, we treat the frequency dependence of $\gamma_{\parallel}$ and $\Delta\gamma_{\parallel}$ approximately by using a power series through second-order in the frequencies,

$$B_{\gamma}(\Omega,T)=B_{\gamma}^{(0)}(T)+\omega_L^2B_{\gamma}^{(2)}(T)+\cdots, \tag{9}$$

$$b(\Omega,T)=\frac{B_{\gamma}^{(0)}(T)+\omega_L^2B_{\gamma}^{(2)}(T)+\cdots}{\gamma_{\parallel}(0)(1+\omega_L^2A+\cdots)}, \tag{10}$$

and

$$\omega_L^2=\omega_0^2=\omega_1^2+\omega_2^2+\omega_3^2.$$

## III. COMPUTATIONAL DETAILS

For the evaluation of the helium and argon dielectric, refractivity, Kerr, and second hyperpolarizability virial coefficients we employ the frequency-dependent interaction induced polarizabilities and second hyperpolarizabilities reported in Part I and in Ref. 3 for the dimers $He_2$ and $Ar_2$.

For $He_2$, this includes FCI results for Dunning's *d*-aug-cc-pVTZ-3321 basis set at 25 internuclear distances in the range of 3.00–13.00 a.u. As discussed in Part I, we added the difference between the CCSD results evaluated with the *d*-aug-cc-pVTZ-3321 and the *d*-aug-cc-pV5Z-3321 basis sets to the FCI results for the interaction induced properties to account for remaining basis set errors. In the following we refer to results obtained using these ''adjusted'' properties as ''extrapolated FCI/*d*-aug-cc-pV5Z'' data.

In Part I we determined for the helium dimer both CCSD(T) and FCI potential energy curves which were shown to be very close to the reference curve determined by Aziz *et al.*[36] in the 3.00–13.00 a.u. internuclear distance range. Nevertheless, in order to reduce the possible sources of inaccuracy, we employed Aziz's potential[36] as $V(R)$ to obtain the results for the virial coefficients of $He_2$ given and discussed in the next section. The dependence of the final results on the choice of the potential energy curve is quite negligible except for the integral of Eq. (1) at low temperatures. As an example, the second dielectric virial coefficients of helium as obtained semiclassically employing our FCI potential energy curve are on the average 1%–2% smaller (in absolute value) at temperatures below 100 K than those obtained employing the Aziz *et al.* potential.[36] The differences are on the order of fractions of a percent at higher temperatures, or for other integrals.

For the $Ar_2$ complex, a *d*-aug-cc-pV5Z-33211 CCSD(T) potential was available[2] and the interaction induced polarizabilities and second hyperpolarizabilities have been computed at the CCSD level with the *d*-aug-cc-pVQZ-33211 (static contributions) and the *d*-aug-cc-pVTZ-33211 (dispersion coefficients) basis sets.[3] The basis set errors in the dispersion coefficients are larger than in the static part. However, this has a negligible influence on the final results, since the dispersion contributions were found in Ref. 3 to be about an order of magnitude smaller than the static terms.[3] The CCSD(T) potential for $Ar_2$, taken from Ref. 2, is available for a total of 59 internuclear distances in the range between 3.8 and 20.0 a.u. The static interaction properties were computed for 12 distances between 5.5 and 30.00 a.u.

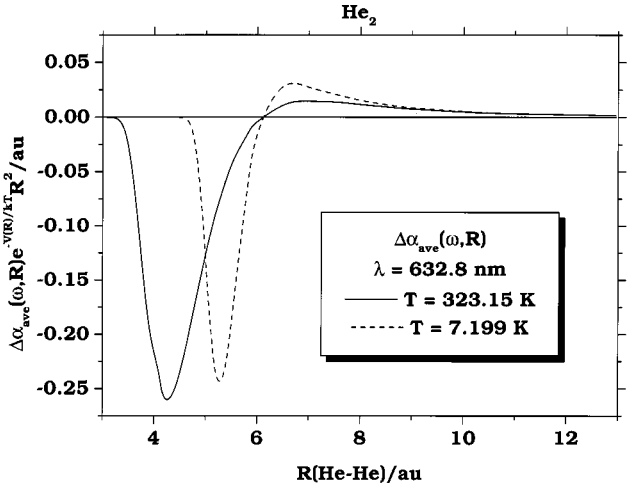



FIG. 1. $He_2$. The function $\Delta\alpha_{ave}(\omega,R)e^{-[V(R)/kT]}R^2$ (a.u.) against the interatomic distance $R$ (a.u.) for $T=323.15$ K and $T=7.199$ K, and for $\lambda=632.8$ nm.

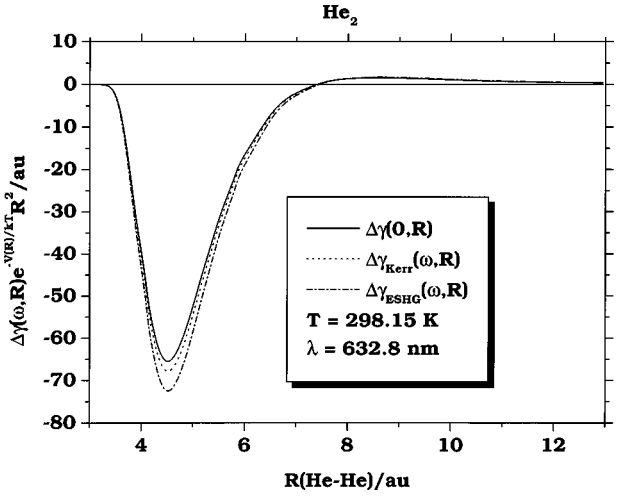



FIG. 2. $He_2$. The function $\Delta\gamma_{\|}(\omega,R)e^{-[V(R)/kT]}R^2$ (a.u.) against the interatomic distance $R$ (a.u.) for $T=298.15$ K and $\lambda=632.8$ nm.

In Ref. 3 we proceeded by a determination of the values of the integrands in Eqs. (1), (4), (5), and (8) for each temperature at the internuclear distances of the *ab initio* calculated interaction properties, followed by a cubic spline interpolation and a numerical integration. Whereas interchanging the first (calculation of the integrand function) and the second (spline interpolation) steps did not lead to appreciable changes in the final results in the case of argon, for the helium dimer the integrand calculation-spline interpolation sequence led to an inaccurate interpolation of the integrand function at the lower end of the integration range. We found that reversing the sequence, i.e., first obtaining cubic spline fits of the interaction induced properties (separately for the static and the frequency-dependent contributions) and *then* determining the integrand functions in a grid of 500 points in the integration range led to a much more stable numerical integration.

The behavior of the integrands involved in the semiclassical determination of the virial coefficients of argon was discussed in some detail in Ref. 3. The changes induced by the use of a larger basis set are not such as to deserve further discussion. The functions were integrated between 5.00 and 30.00 a.u., an interval which was found to be suitable and guaranteed good convergence of the results already in Ref. 3.

The functions which appear as integrands in the evaluation of the second refractivity [Eq. (1)] and the hyperpolarizability [Eqs. (4) and (8)] virial coefficients of helium are displayed in Figs. 1 and 2, respectively.

Figure 1 shows the integrand in Eq. (1) in the 3.00–13.00 a.u. internuclear distance range for both the temperatures of 7.199 K and 323.15 K and for $\lambda=632.8$ nm. The balance between the positive and negative regions of the integrands is not as critical as it was found to be for the $Ar_2$ dimer.[3] The region below $\approx$6 a.u. largely dominates, and it is apparent that the behavior of the function at short range (below 3 a.u.) has no influence on the calculation of the second dielectric and refractivity virial coefficients of helium. As the temperature increases, the integrand is displaced towards the short internuclear distance region, which makes this region more and more important for the description of the property as $T$ increases.

The ''effective'' region of integration becomes more narrow at low temperatures, and the minimum moves toward the equilibrium distance of the dimer (5.61 a.u.). This, together with the previously mentioned fact that the property seems to be more sensitive to the choice of the internuclear potential as $T$ decreases, is an indication that even if minimal, the differences between our FCI potential and the one determined by Aziz (and effectively employed in the calculation of the virial coefficient) are important in the region around equilibrium.

The integrand in the evaluation of the polarizability contribution to the second Kerr [Eqs. (4)] closely resembles the corresponding function seen for argon in Ref. 3. The value of the integrand is far smaller; the maximum, which in $Ar_2$ was larger than 300 a.u., reduces to about 0.15 a.u. for $He_2$. Frequency dispersion is very small, practically undetectable below 4 a.u. or beyond 8 a.u. An effect of frequency dependence is instead observable in Fig. 2, where the integrands corresponding to the polarizability contribution to the second Kerr virial coefficient and to the ESHG second virial coefficient are displayed. Note that—as for Fig. 1—the negative area largely overcomes the positive area lying beyond $\approx$7.5 a.u., and that there is no sign of a quasicancellation effect as seen for the argon dimer.[3]

In order to ascertain the importance of long range effects on the virial coefficients of helium, the 25 extrapolated FCI/*d*-aug-cc-pV5Z frequency-dependent interaction induced polarizabilities and second hyperpolarizabilities were supplemented with a set of points computed using the analytic fits determined in Part I (see Tables VII, VIII and IX in Ref. 1). Twenty three extra points, equally spaced in the 13.0–36.0 a.u. interval were added, and the integration was then extended first from 3.0 a.u. to 27.0 a.u. and then up to 36.0 a.u.

The differences between results obtained with an integration range extended to 27.0 a.u. and 36.0 a.u. are totally negligible. Extending the upper limit of to 36.0 a.u. modifies

TABLE I. Helium. Extrapolated FCI/*d*-aug-cc-pV5Z results for the second dielectric virial coefficient $B_\epsilon(T)$, the dispersion contribution $B_R^{(2)}(T)$ and the second refractivity virial coefficient $B_R(\omega,T)$ at $\lambda=632.8$ nm. The potential used is that of Aziz *et al.* (Ref. 36). Temperatures are in K, virial coefficients in $cm^6\,mol^{-2}$ with frequencies assumed to be given in a.u. We also list the *ab initio* results of Moszynski *et al.* (Ref. 27) for $B_\epsilon$ and experimental data, where available.

| $T$ | $B_\epsilon(T)$ | $B_\epsilon(T)$[a] | $B_\epsilon(T)$ (expt) | Ref. | $B_R^{(2)}(T)$ | $B_R(632.8\text{ nm},T)$ |
|---|---|---|---|---|---|---|
| 3.799 | −0.0731 | −0.0081 | −0.023[b] | 12 | −0.6271 | −0.0763 |
| 4.220 | −0.0549 | −0.0081 | 0.083±0.026 | 4 | −0.4840 | −0.0575 |
| 7.199 | −0.0187 | −0.0092 | −0.036±0.026 | 4 | −0.1892 | −0.0197 |
| 13.804 | −0.0106 | −0.0104 | −0.010±0.026 | 4 | −0.1112 | −0.0112 |
| 20.271 | −0.0105 | −0.0123 | −0.062±0.010 | 4 | −0.1006 | −0.0110 |
| 27.098 | −0.0116 | −0.0144 | −0.088±0.026 | 4 | −0.1001 | −0.0121 |
| 77.400 | −0.0220 | −0.0265 | −0.02±0.02 | 10 | −0.1324 | −0.0226 |
| 100.00 | −0.0262 | | | | −0.1471 | −0.0269 |
| 130.00 | −0.0313 | | | | −0.1651 | −0.0322 |
| 160.00 | −0.0361 | | | | −0.1814 | −0.0370 |
| 180.00 | −0.0390 | | | | −0.1916 | −0.0400 |
| 200.00 | −0.0419 | | | | −0.2012 | −0.0429 |
| 220.00 | −0.0446 | | | | −0.2104 | −0.0456 |
| 242.95 | −0.0475 | −0.0522 | −0.07±0.01 | 10 | −0.2203 | −0.0487 |
| 253.00 | −0.0488 | | | | −0.2245 | −0.0499 |
| 261.00 | −0.0497 | | | | −0.2278 | −0.0509 |
| 274.00 | −0.0513 | | | | −0.2330 | −0.0525 |
| 287.00 | −0.0528 | | | | −0.2380 | −0.0540 |
| 293.00 | −0.0535 | | | | −0.2403 | −0.0547 |
| 296.00 | −0.0538[c] | | | | −0.2415 | −0.0551 |
| 298.15 | −0.0541 | −0.0587 | −0.11±0.02,−0.08 ±0.01 | 6, 7 | −0.2423 | −0.0553 |
| 303.00 | −0.0546 | −0.0592 | −0.059±0.009,−0.06 ±0.01 | 8,11 | −0.2441 | −0.0559[d] |
| 315.00 | −0.0560 | | | | −0.2485 | −0.0573 |
| 322.15 | −0.0567 | −0.0613 | −0.06±0.04 | 5 | −0.2511 | −0.0580 |
| 323.00 | −0.0568 | −0.0614 | −0.068±0.01 | 9 | −0.2514 | −0.0581[e] |
| 323.25 | −0.0569 | −0.0614 | −0.07±0.01 | 10 | −0.2514 | −0.0582 |
| 340.00 | −0.0587 | | | | −0.2573 | −0.0600 |
| 375.00 | −0.0622 | | | | −0.2691 | −0.0636 |
| 407.60 | −0.0654 | | | | −0.2794 | −0.0669 |

[a]Reference 27.
[b]Also −0.030±0.004, Ref. 12 for $^3$He at 4 K.
[c]Cf. −0.0614, calculated at the MP4 level by Bishop and Dupuis (Ref. 24).
[d]Determined as −0.068±0.010 by Achtermann *et al.* (Ref. 11).
[e]Determined as −0.068±0.010 by Achtermann *et al.* (Ref. 9).

the results for the second dielectric and refractivity virial coefficients discussed in Sec. IV A with respect to those obtained integrating to 13.0 a.u. by an average of ≈2.5% at temperatures greater than 100 K. At low temperatures, where the virial coefficients become small in absolute value, the percentage changes are more substantial (≈20% at 27.098 K). The variation is of about 4%–4.5% for the polarizability contribution and of 1%–1.5% for the hyperpolarizability contribution to the second Kerr virial coefficients of Sec. IV B (both static and dispersion). Due to the near cancellation of the two contributions, the percentage effects becomes large in the sum $B_K(\omega,T)$ where this coefficient is small. Finally, for the second hyperpolarizability coefficient, Sec. IV C, the average change is of about 1%–1.5% both for the static and the dispersion contributions. The helium virial coefficients in the tables and figures in Sec. IV are those obtained extending the upper limit of integration in all integrals over the internuclear coordinates up to 36.0 a.u., with a cubic spline grid of 1000 points.

All numerical integrations were carried out with Mathematica.[37] The conversion factors between a.u., SI and esu units are given in the Appendix.

## IV. RESULTS AND DISCUSSION

The results are presented in Tables I–VI and in Figs. 3–6. In the following, we discuss each property separately for both rare gases.

### A. The second dielectric and refractivity virial coefficients

Table I displays the temperature dependence of our extrapolated FCI/*d*-aug-cc-pV5Z results for the second dielectric virial coefficient, $B_\epsilon$, the dispersion contribution $B_R^{(2)}$ and the second refractivity virial coefficient $B_R$ in helium. $B_R$ is evaluated at the wavelength of 632.8 nm. The available experimental data are included in Table I. For $B_\epsilon$ comparison is made with the fully quantum statistical results of Moszynski *et al.*,[27] see also Fig. 1. The range of temperatures extends from 3.799 K up to 407.60 K. In the low temperature

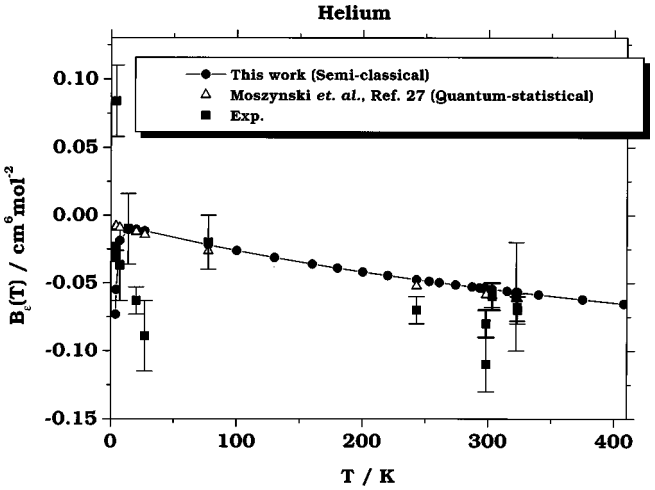



FIG. 3. Helium. Temperature dependence of the second dielectric virial coefficient $B_\epsilon(T)$. Comparison with experiment and with the fully quantum statistical results of Moszynski *et al.* (Ref. 27).

region the semiclassical result, obtained from Eq. (1), corresponds to the zero-order term in a perturbative expansion in orders of $\hbar$.[23,28,32] It has been shown that such an expansion is divergent for very low temperatures, whereas quantum effects altogether are negligible for temperatures greater than 70 K, as Fig. 3 clearly confirms.[28] Comparison with the $B_\epsilon^{(0)}$ results of Moszynski and co-workers is reasonable at temperatures beyond 100 K.[28] At 3.799 K their $B_\epsilon^{(0)}$ is $-0.0961$ $cm^6\,mol^{-2}$, compared to our $-0.0731$ $cm^6\,mol^{-2}$ (cf. quantum statistical result in Table I, $-0.0081$ $cm^6\,mol^{-2}$). Taking into account the level of sophistication of the *ab initio* analysis, the conclusion of Ref. 27 that the measures at some of the low temperature data should be repeated seems plausible. This recommendation may be extended also to the experimental points at higher temperature, which carry error bars that do not enclose the *ab initio* results.

Our result at 296 K is more than 10% less negative than that obtained at the MP4 level by Bishop and Dupuis.[24] Around that temperature, our result is within ≈8% of that of Moszynski *et al.*, which, incidentally, are instead in very good agreement with results (not shown here) obtained with FCI/*d*-aug-cc-pVTZ-33221 data. These differences between the *ab initio* results are a measure of the dependence of the second dielectric virial coefficients on different treatments of electron correlation and on the basis set.

For the second refractivity virial coefficient an experimental value of $-0.068\pm0.010\,cm^6\,mol^{-2}$ has been obtained by Achtermann *et al.*[9,11] at the wavelength of 632.99 nm and for temperatures of 303 and 323 K. Our corresponding results are $-0.0559$ and $-0.0582$ $cm^6\,mol^{-2}$, respectively, and compare reasonably well with experiment. Using a more refined semiclassical approach, see above, Achtermann *et al.* obtained a coefficient of $-0.059$ $cm^6\,mol^{-2}$ at 303 K.

The results for the second dielectric and second refractivity virial coefficients of argon are displayed in Table II. As clearly stated above, in this paper we are not concerned with the frequency dependence of the properties for argon, and we assume the same dispersion contribution as computed in Ref. 3. The *d*-aug-cc-pVQZ-33211 (''*d*QZ'' in Table II and Fig. 5) basis set correction increases the second dielectric coefficients (on the average by 2%–3%). The comparison with experiment is difficult due to the large uncertainty of some of the experimental data. In Ref. 3 we discussed the particular sensitivity of the classical integrals to the balance between positive and negative regions of the integrands in argon, a feature that depends on the temperature and which is practically absent in the case of helium. The changes introduced by the change of basis set are not such as to alter significantly this ratio. This, on the other hand, was shown to be less critical for these properties than for the polarizability contribution to the Kerr constant and for the hyperpolarizability coefficients.[3] As an example, at $T=298.15$ K the ratio between the positive and the negative regions in the integral for $B_\epsilon$ of argon is of about 4:1.

TABLE II. Argon. The second dielectric viral coefficient $B_\epsilon(T)$, the dispersion contribution $B_R^{(2)}(T)$ and the second refractivity viral coefficient $B_R(\omega,T)$ at $\lambda=632.8$ nm. Results with two different basis sets (*d*-aug-cc-pVTZ-33221—*d*TZ below—vs *d*-aug-cc-pVQZ-33221—*d*QZ in the Tables heading) are shown for $B_\epsilon(T)$. The dispersion $[B_R^{(2)}(T)]$ it obtained with the *d*TZ set. The viral refractivity coefficients at the wavelength of 632.8 nm is computed from *d*QZ dielectric contributions plus the *d*TZ dispersion. $T$ is given in K, and the virial coefficients in $cm^6\,mol^{-2}$ with frequencies assumed to be given in a.u.

| $T$ | $B_\epsilon(T)$ *d*TZ | $B_\epsilon(T)$ *d*QZ | $B_R^{(2)}(T)$ *d*TZ | $B_R(632.8\text{ nm},T)$ *d*QZ+*d*TZ |
|---|---|---|---|---|
| 242.95 | 1.4598[a] | 1.4926 | 5.4882 | 1.5211 |
| 253.00 | 1.4410 | 1.4738 | 5.4351 | 1.5020 |
| 261.00 | 1.4268 | 1.4597 | 5.3927 | 1.4877 |
| 273.15 | 1.4066 | 1.4397 | 5.3281 | 1.4673 |
| 274.00 | 1.4053 | 1.4384 | 5.3236 | 1.4660 |
| 287.00 | 1.3852 | 1.4186 | 5.2545 | 1.4458 |
| 293.00 | 1.3765 | 1.4100 | 5.2226 | 1.4371 |
| 296.00 | 1.3722 | 1.4058 | 5.2068 | 1.4328[b] |
| 298.15 | 1.3691[c,d] | 1.4028 | 5.1954[e] | 1.4297[f,g,h] |
| 303.15 | 1.3622[i,j] | 1.3961 | 5.1690 | 1.4229[k] |
| 305.00 | 1.3597[l] | 1.3936 | 5.1592 | 1.4203 |
| 315.00 | 1.3464 | 1.3807 | 5.1067 | 1.4072 |
| 322.00 | 1.3374[m,n,o,p] | 1.3720 | 5.0701 | 1.3983[q] |
| 340.00 | 1.3155 | 1.3509 | 4.9768 | 1.3767 |
| 370.00 | 1.2770 | 1.3143 | 4.7991 | 1.3392 |
| 407.60 | 1.2449[r] | 1.2842 | 4.6383 | 1.3082 |

[a]Expt, $1.84\pm0.07$. Ref. 10.
[b]Expt, 2.52(34), $\lambda=594.096$ nm—1.73(34), $\lambda=543.516$ nm—1.81(34), $\lambda=325.530$ nm, $T=296.82$ K, Ref. 42.
[c]Calc 1.53, at 300 K, Ref. 19.
[d]Expt $0.79\pm0.10$, Ref. 6.
[e]Calc 9.41, at 300 K, Ref. 19.
[f]Expt, $1.57\pm0.58$, $\lambda=632.8$ nm—$1.55\pm0.74$, $\lambda=514.5$ nm—$1.58\pm0.69$, $\lambda=488.0$ nm—$1.53\pm0.32$, $\lambda=457.9$ nm, $T=298.2$ K, Ref. 43.
[g]Expt, $2.16\pm0.34$, $T=298.2$ K, $\lambda=632.99$ nm, Ref. 44.
[h]Expt, $1.49\pm0.15$, at 298.2 K, $\lambda=632.99$ nm, Ref. 45.
[i]Expt, $1.22\pm0.09$, Ref. 10.
[j]Expt, $1.23\pm0.05$, Ref. 46.
[k]Expt, $1.75\pm0.05$, $\lambda=632.99$ nm, Ref. 11.
[l]Expt, $1.0\pm2.1$, $T=306.15$ K, Ref.47.
[m]Calc, (SCF) 0.48, Ref. 18.
[n]Expt, $0.39\pm0.20$, Ref. 5.
[o]0.726 from CIS measurements, Ref. 48.
[p]Expt, $0.72\pm0.13$, at 323 K, Ref. 49.
[q]Expt, $1.76\pm0.05$, $T=323$ K, $\lambda=632.99$ nm, Ref. 9.
[r]Expt, $0.1\pm0.3$, Ref. 10.

TABLE III. Helium. The second Kerr viral coefficient $B_K(\omega,T)=B_K^{\alpha}(\omega,T)+B_K^{\gamma}(\omega,T)$. The two contributions are further expanded as $B_K^{\alpha}(\omega,T)=B_K^{(0),\alpha}(T)+\omega^2 B_K^{(2),\alpha}(T)$ and $B_K^{\gamma}(\omega,T)=B_K^{(0),\gamma}(T)+2\omega^2 B_K^{(2),\gamma}(T)$. $B_K(\omega,T)$ is also given for the wavelength of 632.8 nm. $T$ is given in Kelvin, and virial coefficients in $V^{-2}\,m^8\,mol^{-2}\times10^{-36}$ with frequencies assumed to be given in a.u.

| $T$ | $B_K^{(0),\alpha}(T)$ | $B_K^{(2),\alpha}(T)$ | $B_K^{(0),\gamma}(T)$ | $B_K^{(2),\gamma}(T)$ | $B_K$(632.8 nm) |
|---|---|---|---|---|---|
| 77.400 | 10.5336 | 21.3451 | −2.0979 | −8.6081 | 8.4572 |
| 100.000 | 8.2653 | 16.6453 | −2.2240 | −8.9982 | 6.0343 |
| 130.000 | 6.4822 | 12.9635 | −2.3794 | −9.4879 | 4.0716 |
| 160.000 | 5.3644 | 10.6643 | −2.5204 | −9.9347 | 2.7963 |
| 180.000 | 4.8230 | 9.5541 | −2.6070 | −10.2096 | 2.1596 |
| 200.000 | 4.3874 | 8.6630 | −2.6885 | −10.4678 | 1.6353 |
| 220.000 | 4.0288 | 7.9311 | −2.7653 | −10.7110 | 1.1936 |
| 242.950 | 3.6878 | 7.2367 | −2.8482 | −10.9732 | 0.7634 |
| 253.000 | 3.5572 | 6.9713 | −2.8829 | −11.0829 | 0.5956 |
| 261.000 | 3.4602 | 6.7742 | −2.9098 | −11.1681 | 0.4697 |
| 274.000 | 3.3141 | 6.4779 | −2.9525 | −11.3027 | 0.2780 |
| 287.000 | 3.1808 | 6.2077 | −2.9938 | −11.4329 | 0.1006 |
| 293.000 | 3.1230 | 6.0909 | −3.0124 | −11.4915 | 0.0230 |
| 296.000 | 3.0950 | 6.0342 | −3.0216 | −11.5205 | −0.0148 |
| 298.150 | 3.0752 | 5.9942 | −3.0282 | −11.5412 | −0.0415 |
| 303.000 | 3.0317 | 5.9061 | −3.0429 | −11.5874 | −0.1007 |
| 315.000 | 2.9293 | 5.6993 | −3.0785 | −11.6994 | −0.2409 |
| 322.150 | 2.8718 | 5.5833 | −3.0993 | −11.7646 | −0.3205 |
| 323.000 | 2.8652 | 5.5698 | −3.1017 | −11.7723 | −0.3297 |
| 323.150 | 2.8640 | 5.5674 | −3.1021 | −11.7736 | −0.3314 |
| 340.000 | 2.7383 | 5.3141 | −3.1496 | −11.9228 | −0.5074 |
| 375.000 | 2.5118 | 4.8583 | −3.2430 | −12.2153 | −0.8327 |
| 407.600 | 2.3341 | 4.5019 | −3.3242 | −12.4690 | −1.0960 |

### B. The second Kerr virial coefficients

As discussed in Sec. I, in experimental studies even as recent as 1992 no appreciable deviations from the linear dispersion law with the density has been detected for the Kerr constant of helium.[14,15] The contributions to the second Kerr virial coefficient of helium are reported in Table III and shown in Fig. 4. The coefficients $B_K$ are evaluated for the wavelength of 632.8 nm. The range of temperatures extends from 77.40 K to 407.60 K. We computed the coefficients also at low temperature, and observed that—as it could be expected—the polarizability contribution $B_K^{\alpha}$ becomes rapidly dominant, being at 3.799 K two order of magnitude larger than the one computed at 77.4 K, and about 500 times larger than the contribution at 303 K. The increase is one order of magnitude ''slower'' for the hyperpolarizability contribution. Due to near cancellation of the two contributions ($B_K^{\alpha}$ and $B_K^{\gamma}$), the ratio for the actual Kerr virial coefficient $B_K$ at 3.799 K and 303 K is if ≈10 000. Bruch *et al.*[23] estimated from their quantum statistical analysis that the ratio of $B_K^{\alpha}$(4.2 K) and $B_K^{\alpha}$(300 K) should be of ≈39. At 300 K the authors obtain, through a coupled perturbed Hartree–Fock approach, a value of $2.56\times10^{-36}\,V^{-2}\,m^8\,mol^{-2}$ for their $B_K$, which includes however only the polarizability term. Our result at 300 K lies around $2.7\times10^{-36}\,V^{-2}\,m^8\,mol^{-2}$, in reasonable agreement with the estimate by Bruch *et al.*[23] In conclusion, the frequency dependence of $B_K$ for helium is quite negligible in the whole range of temperatures, and the near cancellation of the polarizability contribution with the hyperpolarizability contribution leads to predict that there is a temperature (our estimate is around 295 K) where the second Kerr virial coefficient of helium goes to zero. There is thus a striking difference with respect to what is seen for argon, where $X_K^{\alpha}$ is two orders of magnitude larger than $X_K^{\gamma}$ and clearly dominates $B_K$ up to very high temperatures.

In Table IV we list the results, both the different contributions and the overall coefficient, for the second Kerr virial coefficient of argon evaluated at a wavelength of 458.0 nm. The comparison with experiment[38] is central to the scope of Fig. 5. Improving the basis set has minor effects on the polarizability anisotropy contribution, whereas the hyperpolarizability term changes substantially. Since the total coefficient is dominated by the polarizability contribution, the overall variation is in the order of about a 3%. The experimental second Kerr virial coefficients by Dunmur *et al.*[38] at 458 nm for several temperatures carry large error bars, which nevertheless do not include either of our results (cf. Fig. 5). The current *d*QZ results are only slightly closer to these experimental values than the previous *d*TZ estimates.[3] On the other hand, if we consider the much more recent Kerr study of Shelton and Palubinskas,[39] and as in Ref. 3 compute the ratio $b_{\rm fit}/a_{\rm fit}$ of the virial expansion $\gamma_{\rm eff}^K=a_{\rm fit}+b_{\rm fit}\rho$ from the dc-Kerr hyperpolarizability at $\lambda=632.8$ nm which is taken from Ref. 39 ($77.8\times10^{-63}\,C^4\,m^4\,J^{-3}\approx1248$ a.u.) and from our new value of $B_K$ at 632.8 nm ($5.57\times10^{-33}\,V^{-2}\,m^8\,mol^{-2}$), we obtain a value of $8.70\times10^{-5}\,m^3\,mol^{-1}$ at 296 K. This compares very favorably with the experimental measurement ($b_{\rm fit}/a_{\rm fit}=8.9\pm0.3\times10^{-5}\,m^3\,mol^{-1}$ at $\lambda=632.8$ nm and $T=296.15$ K).

The neat dominance of the contribution arising from the integration in Eq. (4) with respect to that arising from the Kerr interaction hyperpolarizability and which is related to the integral in Eq. (5), rules out possible causes of inaccuracies in our numbers due to the critical balance of positive and negative contributions to the hyperpolarizability classical integrals mentioned above. Also, the neglect of long range effects [i.e., having limited the integration in Eq. (4) to 30 a.u.] is of no consequence for our conclusions; at 298.15 K,

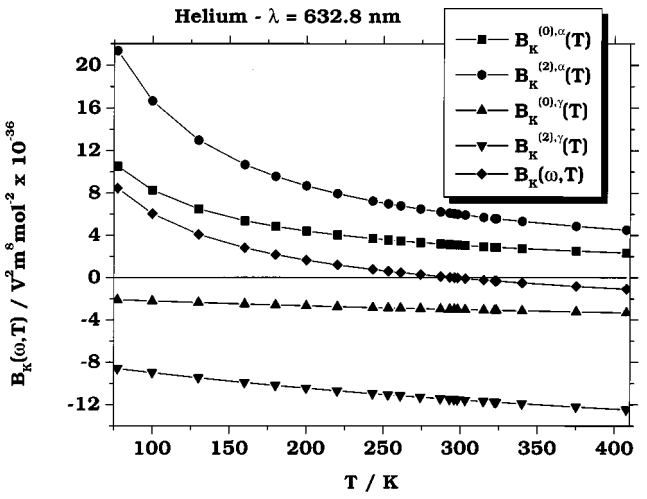



FIG. 4. Helium. Temperature dependence of the second Kerr virial coefficient $B_K(\omega,T)=B_K^{\alpha}(\omega,T)+B_K^{\gamma}(\omega,T)$. Also, $B_K^{\alpha}(\omega,T)=B_K^{(0),\alpha}(T)+\omega^2 B_K^{(2),\alpha}(T)$ and $B_K^{\gamma}(\omega,T)=B_K^{(0),\gamma}(T)+2\omega^2 B_K^{(2),\gamma}(T)$. The second Kerr virial coefficient is shown for a wavelength $\lambda=632.8$ nm.

TABLE IV. Argon. The second Kerr viral coefficient $B_K(\omega,T)=B_K^{\alpha}(\omega,T)+B_K^{\gamma}(\omega,T)$. The two contributions are further expanded as $B_K^{\alpha}(\omega,T)=B_K^{(0),\alpha}(T)+\omega^2 B_K^{(2),\alpha}(T)$ and $B_K^{\gamma}(\omega,T)=B_K^{(0),\gamma}(T)+2\omega^2 B_K^{(2),\gamma}(T)$. The static contributions are computed with the *d*-aug-cc-pVQZ-33221 (dQZ) set, whereas the dispersion is obtained with the smaller *d*-aug-cc-pVTZ-33221 (dTZ) basis set. $B_K(\omega,T)$ as obtained from the results for the two contributions is given for $\lambda=458$ nm. $T$ is given in Kelvin, and the virial coefficients in $V^{-2}\,m^8\,mol^{-2}$ with frequencies assumed to be given in a.u.

| | $B_K^{(0),\alpha}(T)$ $\times 10^{33}$ | $B_K^{(2),\alpha}(T)$ $\times 10^{33}$ | $B_K^{(0),\gamma}(T)$ $\times 10^{35}$ | $B_K^{(2),\gamma}(T)$ $\times 10^{35}$ | $B_K(458.0\,\text{nm},T)$ $\times 10^{33}$ | $\times 10^{33}$ |
|---|---|---|---|---|---|---|
| $T$ | *d*QZ | *d*TZ | *d*QZ | *d*TZ | dQZ+dTZ | Expt. from Ref. 38 |
| 242.95 | 7.0613 | 34.8792 | 2.1983 | −29.5492 | 7.7678 | |
| 253.00 | 6.7123 | 33.1552 | 2.2944 | −27.7828 | 7.3860 | 5.4±0.9 |
| 261.00 | 6.4588 | 31.9027 | 2.3611 | −26.5227 | 7.1086 | 4.9±0.9 |
| 273.15 | 6.1093 | 30.1757 | 2.4482 | −24.8213 | 6.7262 | |
| 274.00 | 6.0863 | 30.0621 | 2.4537 | −24.7110 | 6.7010 | 4.3±0.7 |
| 287.00 | 5.7555 | 28.4276 | 2.5299 | −23.1477 | 6.3389 | 4.0±0.7 |
| 293.00 | 5.6151 | 27.7333 | 2.5603 | −22.4984 | 6.1852 | 3.9±0.7 |
| 296.00 | 5.5474 | 27.3992 | 2.5745 | −22.1892 | 6.1111 | |
| 298.15 | 5.5000 | 27.1648 | 2.5843 | −21.9737 | 6.0592 | |
| 303.15 | 5.3929 | 26.6354 | 2.6058 | −21.4911 | 5.9419 | |
| 305.00 | 5.3543 | 26.4449 | 2.6134 | −21.3190 | 5.8997 | 3.8±0.7 |
| 315.00 | 5.1555 | 25.4620 | 2.6506 | −20.4438 | 5.6819 | 3.8±0.7 |
| 322.00 | 5.0251 | 24.8178 | 2.6733 | −19.8828 | 5.5392 | |
| 340.00 | 4.7194 | 23.3066 | 2.7210 | −18.6100 | 5.2042 | |
| 375.00 | 4.2233 | 20.8549 | 2.7787 | −16.6952 | 4.6606 | |
| 407.60 | 3.8497 | 19.0089 | 2.8027 | −15.4031 | 4.2509 | |

when we carry out the integration for $X_K^{\alpha}$ in a interval reduced by 10% (i.e., up to 28.8 a.u. instead of 30 a.u.), the integral is reduced by ≈0.08%.

In conclusion the experimental Kerr data of Dunmur *et al.*[38] are most likely inaccurate, and should therefore be re-examined.

### C. The second hyperpolarizability virial coefficients

The results for the helium hyperpolarizability virial coefficients are given in Table V and Fig. 6. Once again, the range of temperatures goes from 77.4 K to 407.60 K, but we have results also for lower temperatures. Due to the absence of a proper quantum statistical treatment, we refrain from discussing them at this stage. The dispersion contribution is far more important here than for the former coefficients. At 296 K Bishop and Dupuis[24] determined the static $b$ [Eq. (10)] at the MP4 level as $-1.41\ cm^3\,mol^{-1}$. This compares reasonably well with our corresponding static result of

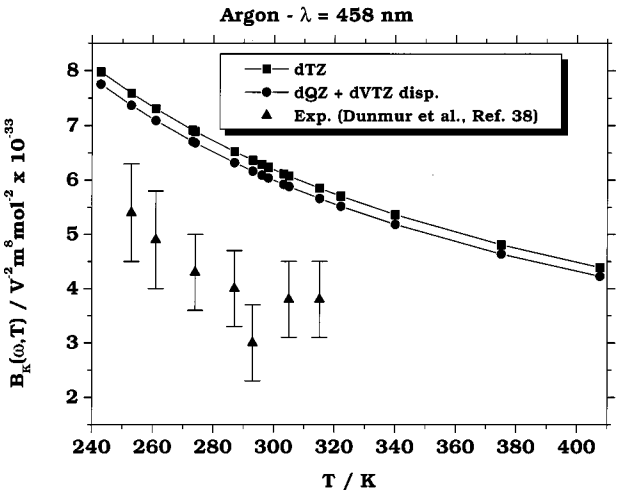



FIG. 5. Argon. Temperature dependence of the second Kerr virial coefficient $B_K(\omega,T)$ for $\lambda=458$ nm. Comparison of results of Ref. 3—obtained with the *d*-aug-cc-pVTZ (*d*TZ) basis set—and of experiment (Ref. 38) with the current *d*-aug-cc-pVQZ (static)+*d*-aug-cc-pVTZ (dispersion) results.

TABLE V. Helium. The second hyperpolarizability virial coefficient. $B_{\gamma}^{(0)}(T)$, $B_{\gamma}^{(2)}(T)$, and $b(\Omega,T)$ for an ESHG process ($\omega_1=\omega_2=\omega,\omega_3=0,\omega_L^2=6\omega^2$) at 632.8 nm as a function of temperature (Kelvin). To compute $b$, we assumed $\gamma_{\parallel}(-2\omega;\omega,\omega,0)=43.104$ a.u., as obtained by Bishop and Pipin (Ref. 50). $B_{\gamma}$ is given in $C^4\,m^7\,J^{-3}\,mol^{-1}\times 10^{-68}$ and $b$ in $cm^3\,mol^{-1}$. Frequencies are assumed to be given in a.u.

| $T$ | $B_{\gamma}^{(0)}(T)$ | $B_{\gamma}^{(2)}(T)$ | $b(632.8\,\text{nm},T)$ |
|---|---|---|---|
| 77.40 | −0.2498 | −1.0252 | −1.0482 |
| 100.00 | −0.2649 | −1.0716 | −1.1095 |
| 130.00 | −0.2834 | −1.1299 | −1.1851 |
| 160.00 | −0.3002 | −1.1831 | −1.2537 |
| 180.00 | −0.3105 | −1.2159 | −1.2959 |
| 200.00 | −0.3202 | −1.2466 | −1.3356 |
| 220.00 | −0.3293 | −1.2756 | −1.3729 |
| 242.95 | −0.3392 | −1.3068 | −1.4133 |
| 253.00 | −0.3433 | −1.3199 | −1.4302 |
| 261.00 | −0.3465 | −1.3300 | −1.4433 |
| 274.00 | −0.3516 | −1.3461 | −1.4640 |
| 287.00 | −0.3565 | −1.3616 | −1.4841 |
| 293.00 | −0.3588 | −1.3686 | −1.4932 |
| 296.00 | −0.3599 | −1.3720 | −1.4977[a] |
| 298.15 | −0.3606 | −1.3745 | −1.5009 |
| 303.00 | −0.3624 | −1.3800 | −1.5080 |
| 315.00 | −0.3666 | −1.3933 | −1.5253 |
| 322.15 | −0.3691 | −1.4011 | −1.5354 |
| 323.00 | −0.3694 | −1.4020 | −1.5366 |
| 323.15 | −0.3694 | −1.4021 | −1.5368 |
| 340.00 | −0.3751 | −1.4199 | −1.5599 |
| 375.00 | −0.3862 | −1.4547 | −1.6053 |
| 407.60 | −0.3959 | −1.4850 | −1.6448 |

[a]Bishop and Dupuis (Ref. 24) determined MP4 static $b=-1.41\ cm^3\,mol^{-1}$.

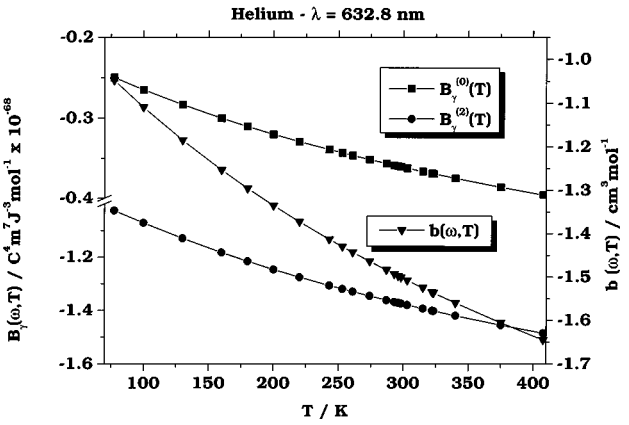



FIG. 6. Helium. Temperature dependence of the second hyperpolarizability virial coefficients $B_\gamma^{(0)}(T)$, $B_\gamma^{(2)}(T)$, and $b(\omega,T)$ for an ESHG process ($\omega_1=\omega_2=\omega$; $\omega_3=0$, $\omega_L^2=6\omega^2$) at $\lambda=632.8$ nm.

$-1.3349\ \mathrm{cm^3\,mol^{-1}}$. The lack of experimental data prevents a further discussion of our results for $b$ of the individual gases. The behavior of the integrand in Fig. 2 is—at all temperatures—very smooth, with the negative contribution to the integral in Eq. (8) largely dominating the positive contribution.

In Table VI we summarize the results for the second hyperpolarizability virial coefficient of argon. The static contribution changes considerably going from the *d*-aug-cc-pVTZ-33211 to the *d*-aug-cc-pVQZ-33211 basis set. As a consequence a significant change is seen in the $b(\omega,T)$ results. No experimental data are available for $B_\gamma$, but using the same procedure as in our previous paper,[3] we can estimate the quantity $b(\mathrm{ArH_2})+b(\mathrm{H_2He})$. At $\lambda=514.5$ nm and at $T=298$ K we obtain $b=0.188\ \mathrm{cm^3\,mol^{-1}}$ for argon and $b=-1.58\ \mathrm{cm^3\,mol^{-1}}$ for helium. The ratios $\gamma(\mathrm{Ar})/\gamma(\mathrm{H_2})$ and $\gamma(\mathrm{H_2})/\gamma(\mathrm{He})$ as a function of the gas density were measured by Donley and Shelton.[21] Combining these data, we compute $b(\mathrm{ArH_2})+b(\mathrm{H_2He})=23.20\ \mathrm{cm^3\,mol^{-1}}$, in contrast to the experimental value $-1.4\pm8.0\ \mathrm{cm^3\,mol^{-1}}$.[21]

TABLE VI. Argon. The second hyperpolarizability virial coefficient. $B_\gamma^{(0)}(T)$, $B_\gamma^{(2)}(T)$, $B_\gamma(T)$, and $b(\omega,T)$ for the ESHG process ($\omega_1=\omega_2=\omega,\omega_3=0,\omega_L^2=6\omega^2$) at $\lambda=514.5$ nm as a function of temperature (Kelvin). To compute $b$, we used $\gamma_{\|}(-2\omega;\omega,\omega,0)=1577$ a.u. (Ref. 51). Static results are obtained with the *d*-aug-cc-pVQZ-33221 (*d*QZ) basis set, whereas the frequency dispersion was that computed using a *d*-aug-cc-pVTZ-33221 (*d*TZ) basis set. $B_\gamma$ is given in $\mathrm{C^4\,m^7\,J^{-3}\,mol^{-1}}\times10^{-68}$ and $b$ in $\mathrm{cm^3\,mol^{-1}}$. Frequencies are assumed to be given in a.u.

| $T$ | $B_\gamma^{(0)}(T)$ *d*QZ | $B_\gamma^{(2)}(T)$ *d*TZ | $B_\gamma(T)$ *d*QZ+*d*TZ | $b(514.5\ \mathrm{nm},T)$ *d*QZ+*d*TZ |
|---|---|---|---|---|
| 242.95 | 2.6179 | −35.1908 | 0.9620 | 0.0978 |
| 253.00 | 2.7324 | −33.0872 | 1.1755 | 0.1195 |
| 261.00 | 2.8119 | −31.5865 | 1.3256 | 0.1348 |
| 273.15 | 2.9156 | −29.5603 | 1.5247 | 0.1551 |
| 274.00 | 2.9222 | −29.4289 | 1.5374 | 0.1564 |
| 287.00 | 3.0129 | −27.5671 | 1.7157 | 0.1745 |
| 293.00 | 3.0492 | −26.7939 | 1.7883 | 0.1819 |
| 296.00 | 3.0661 | −26.4257 | 1.8226 | 0.1853 |
| 298.15 | 3.0777 | −26.1690 | 1.8463 | 0.1878[a] |
| 303.15 | 3.1033 | −25.5943 | 1.8990 | 0.1931 |
| 305.00 | 3.1123 | −25.3892 | 1.9176 | 0.1950 |
| 315.00 | 3.1566 | −24.3470 | 2.0110 | 0.2045 |
| 322.00 | 3.1837 | −23.6789 | 2.0695 | 0.2105 |
| 340.00 | 3.2405 | −22.1631 | 2.1976 | 0.2235 |
| 375.00 | 3.3092 | −19.8827 | 2.3736 | 0.2414 |
| 407.60 | 3.3378 | −18.3439 | 2.4747 | 0.2517 |

[a]The static value is 0.8074, which can be compared to the estimated value of $-29.8\pm10.8$, Ref. 24, obtained from the *ab initio* result of He and the experimental density ratios of Ref. 21.

In Ref. 3 we made a conservative estimate of the changes expected in the integral $X_\gamma$ for argon at 298.15 K based upon improving the basis set from triple-zeta to quadruple-zeta quality. We made this prediction considering the balance of negative and positive regions and its effect on the result in Eq. (8). We predicted a possible change of sign and a decrease of about one order of magnitude in $B_\gamma(\omega,T)$ and $b$. The integral (which at $T=298.15$ K and $\lambda=514.5$ nm was $\approx24\,000$ a.u., and was predicted to change to $\approx -2000$ a.u.) becomes instead $\approx11000$ a.u. Thus, our prediction was certainly conservative, but the effect remains impressive.

## V. CONCLUSIONS

We have carried out a detailed study of the second dielectric, refractive, Kerr, and hyperpolarizability virial coefficients of helium and argon. Our study, which assumes the validity of a semiclassical approach, is extended to a wide range of temperatures and employs the FCI and CCSD results for the frequency-dependent interaction induced polarizabilities and hyperpolarizabilities for $\mathrm{He_2}$ and $\mathrm{Ar_2}$, respectively, which were reported in Refs. 1 and 3. We compare our virial coefficients with those obtained in other recent *ab initio* calculations and with the available experimental data.

The present results for the second dielectric virial coefficient of helium are in reasonable agreement with a recent quantum perturbation study of Moszynski *et al.*,[28] and the fully quantum statistical results of Ref. 27 in the range of temperatures between 70 and 410 K. For the second refractivity virial coefficient of helium our study is the first report of a theoretical determination based on *ab initio* results for the frequency-dependence of the interaction induced polarizability of $\mathrm{He_2}$. For temperatures higher than 70 K the agreement with most of the experimental data is satisfactory. This is also the case for the very few experimental data for the refractivity virial coefficient.

For the second dielectric virial coefficients for argon we obtain results which are about 3% larger than the values obtained in a previous study[3] where we employed a smaller basis set in the calculation of the interaction induced polarizability of $\mathrm{Ar_2}$. Since this is a small change compared to the error bar and the scattering of the experiment results, it makes no significant effect on the agreement between the theoretical and experimental results, which is reasonably good for the temperature range between 242 and 303 K, but unsatisfactory for higher temperatures.

For the Kerr constant of helium the very weak quadratic dependence on the gas density is confirmed; in fact, around room temperature the second Kerr virial coefficient—whose frequency dependence is negligible—practically vanishes. This explains the difficulties the experimentalists still en-

counter in detecting any deviations from the linear pressure dependence of ${}_mK$.

For the second Kerr virial coefficient of argon, the improved calculations for the interaction induced polarizability and hyperpolarizability of $Ar_2$ reduced the theoretical results for $B_K$ by about 3%. Our results of $8.70\times10^{-5}\,m^3\,mol^{-1}$ for $B_K/A_K$ at 632.8 nm and 296.15 K is in favorable agreement with the recent accurate experimental Kerr result of $(8.9\pm0.3)\times10^{-5}\,m^3\,mol^{-1}$ which was obtained by Shelton and Palubinskas.[39] The present calculations substantiate the significant disagreement with earlier experimental results for 458 nm by Dunmur *et al.*[38] found in Ref. 3. We suggest therefore an experimental reinvestigation of the latter results.

As anticipated in Ref. 3, the reevaluation of the interaction induced second hyperpolarizability of $Ar_2$ leads to a significant change in the theoretical results for the relative hyperpolarizability second virial coefficient $b(\omega,T)$ of argon—at 298 K and 514.5 nm from 0.6822 $cm^3\,mol^{-1}$ to 0.1878 $cm^3\,mol^{-1}$.

Combining the present results for $b$ for argon and helium with the pressure ratios employed in the experimental determination of $b(ArH_2)$ and $b(HeH_2)$, we obtain a theoretical estimate for $b(ArH_2)+b(HeH_2)$ of 23.2 $cm^3\,mol^{-1}$, which is even less in agreement with the experimental value from Ref. 21 of $-1.4\pm8.0\,cm^3\,mol^{-1}$, than the previous theoretical result of Ref. 3. The remaining discrepancy between the theoretical and the experimental result can likely not be explained by shortcomings in the *ab initio* results for $\Delta\gamma_{\|}$ of $He_2$ and $Ar_2$, since the present calculations account for the frequency-dependence of the interaction induced hyperpolarizability of both $He_2$ and $Ar_2$ and they are—in particular for $He_2$—essentially converged with respect to the one-particle basis sets and the correlation treatment. More likely they are due to either the neglect of quantum effects in the calculation of the hyperpolarizability virial coefficients[23] or to approximations made in the comparison with the experiment, e.g., in the ansatz for the (pressure-dependent) local field factors.[21]

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## APPENDIX: CONVERSION FACTORS

Conversion factors from atomic units to SI and esu.[40] See also Ref. 41.

(1) 1 a.u. of $\rho\equiv a_0^{-3}\,mol\cong6.74833\times10^{30}\ m^{-3}\,mol=6.74833\times10^{24}\ cm^{-3}\,mol$ (esu);
(2) 1 a.u. of $\omega\equiv\hbar a_0^{-2}m_e^{-1}\cong4.13414\times10^{16}\ s^{-1}$;
(3) 1 a.u. of $\alpha\equiv e^2a_0^4m_e\hbar^{-2}\cong1.64878\times10^{-41}\ C^2\,m^2\,J^{-1}=1.48186\times10^{-25}\ cm^3$ (esu);
(4) 1 a.u. of $\gamma\equiv e^4a_0^{10}m_e^3\hbar^{-6}\cong6.23538\times10^{-65}\ C^4\,m^4\,J^{-3}=5.03669\times10^{-40}$ esu;
(5) 1 a.u. of $A_R(\omega,T)$, $b\equiv a_0^3\,mol^{-1}\cong1.48135\times10^{-31}\ m^3\,mol^{-1}=1.48135\times10^{-25}\ cm^3\,mol^{-1}$ (esu);
(6) 1 a.u. of $B_R(\omega,T)\equiv a_0^6\,mol^{-2}\cong2.19587\times10^{-62}\ m^6\,mol^{-2}=2.19587\times10^{-50}\ cm^6\,mol^{-2}$ (esu);
(7) 1 a.u. of ${}_mK(\omega,T)$, $A_K(\omega,T)\equiv e^2a_0^9m_e^2\,mol^{-1}\hbar^{-4}\cong5.60408\times10^{-55}\ V^{-2}\,m^5\,mol^{-1}=5.03672\times10^{-40}$ esu;
(8) 1 a.u. of $B_K(\omega,T)\equiv e^2a_0^{12}m_e^2\,mol^{-2}\hbar^{-4}\cong8.30439\times10^{-86}\ V^{-2}\,m^8\,mol^{-2}=7.46365\times10^{-65}$ esu;
(9) 1 a.u. of $B_\gamma(\omega_0,\omega_1,\omega_2,\omega_3,T)\equiv e^4a_0^{13}m_e^3\,mol^{-1}\hbar^{-6}\cong9.23988\times10^{-96}\ C^4\,m^7\,J^{-3}\,mol^{-1}=7.46361\times10^{-65}$ esu.

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