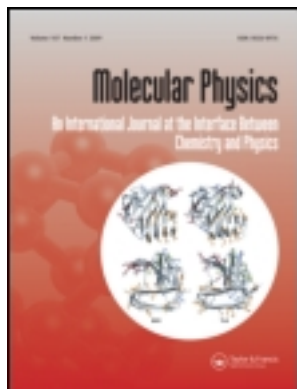


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# Accurate *ab initio* potential for argon dimer including highly repulsive region

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An *ab initio* potential has been developed for the argon dimer. This potential is based on coupled-cluster calculations with single, double, and non-iterated triple excitations in a sequence of very large basis sets, up to augmented sextuple-zeta quality and containing bond functions, followed by extrapolations to the complete basis set limit. The calculations included intermolecular distances as small as 0.25 Å, where the interaction potential is of the order of 4 keV. The computed points were fitted by an analytic expression. The new potential has the minimum at 3.767 Å with a depth of 99.27 cm<sup>-1</sup> respectively, very close to experimental values of 3.761 ± 0.003 Å and 99.2 ± 1.0 cm<sup>-1</sup> respectively. The potential was used to compute the spectra of the argon dimer and the virial coefficients. The latter calculations suggest a possible revision of the established experimental reference results. From the agreement achieved with experimental values and from comparisons of the fit with available piecewise information on specific regions of the argon–argon interaction, one can assume that the present work provides the best overall representation of the true argon–argon potential to date.

## 1. Introduction

The properties of rare gases have always been of great interest to both experimentalists and theorists. Argon has received a substantial share of this interest because of its abundance in the atmosphere. The properties of argon are determined mainly by the interaction between a pair of argon atoms, although pair-nonadditive effects have to be included for quantitative predictions in condensed phase [1–4]. Like other weakly bound complexes, the argon dimer presents a difficult challenge for *ab initio* calculations since one must use both highly correlated electronic structure methods and large basis sets, including a significant number of polarization and diffuse functions, to obtain a potential energy curve of an acceptable accuracy. On the other hand, the large number of electrons in the argon dimer make the *ab initio* calculations significantly more demanding than, e.g., for the helium dimer, for which the state-of-the-art *ab initio* potentials are close to reaching millikelvin accuracy [5–7] and are now enabling one to refine existing thermophysical standards [8, 9]. Since argon is another benchmark system in thermal physics,

improvements of the accuracy of the argon dimer potential are of great importance.

The 1993 empirical argon–argon HFDID1 potential of Aziz [10] is generally assumed to be the most accurate one available. This potential, in a Hartree-Fock plus individually damped dispersion form [11], has been fitted to accurately reproduce a number of macro- and microscopic properties of argon. However, the Aziz potential does not predict all of the quantities that have been measured to within the experimental error bars [12]. Even more significant problems can be expected for properties that depend on the strongly repulsive part of the potential [13]. For these properties it may be more appropriate to use the older, 1990 empirical HFD-B3 or HFDTCS2 potentials of Aziz and Slaman [14], which were constructed with an emphasis on the reproduction of the repulsive wall. Still, these potentials, as shown by Phelps *et al.* [13], are not able to provide reasonable predictions for the collision and viscosity cross-section data [15–17] sensitive to very high energies (up to 10 keV, which, roughly speaking, corresponds to the probing of the argon–argon potential for distances starting from 0.25 Å). Notice also that HFDID1 was not intended to be used to predict properties that depend strongly on the repulsive wall and its performance for the whole set of data on which HFD-B3 and HFDTCS2

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were fitted/tested is unknown. Thus, there is even no single potential that can be recommended for the whole range of interatomic separations. It is evident, therefore, that a new potential is needed that accurately describes the highly repulsive region of the argon–argon interaction and is a good representation of the true potential in all other regions as well.

Highly correlated *ab initio* calculations of the interaction energies for the argon dimer have become possible thanks to many-body perturbation theory (MBPT) and coupled-cluster methods developed by Bartlett and collaborators [18–39]. The first such calculations were attempted as early as 1987 [40] using the fourth-order MBPT (MBPT4) level. However, these MBPT4 calculations underestimated the van der Waals well depth by 25% compared to the Aziz potential [10], mainly due to the lack of high angular functions (higher than  $f$ ) in the basis set. A year later, McLean *et al.* [41] reduced the error in well depth to 15% using the interacting correlated fragments (ICF) approach. More accurate calculations have been made possible by the introduction of the augmented correlation-consistent (aug-cc-pVnZ) basis sets by Dunning and coworkers [42, 43] and by the use of the complete basis set (CBS) extrapolation techniques. Using the coupled-cluster approach with single, double and noniterative triple excitations (CCSD(T)) and the CBS extrapolation from calculations in basis sets up to d-aug-cc-pVQZ, Woon [44] obtained an argon–argon potential that was  $\sim 5\%$  too shallow. These calculations were later extended to basis sets up to d-aug-cc-pV6Z, with the correction for the core and core-valence correlation taken into account, reducing the error in the well depth to  $\sim 3\%$  [45].

Further advancement in the accuracy of the *ab initio* argon–argon potentials has been made possible by the use of bond functions [46–48] which provide a most efficient way of saturating the dispersion component of the interaction energy [49, 50]. The first calculations of the argon–argon potential using bond functions (and the MBPT4 method) were carried out by Tao and Pan [51]. The resulting well depth was 8% too small. More recently, Fernandez and Koch [58] added a set of ( $3s3p2d1f1g$ ) midbond functions to the d-aug-cc-pV5Z basis set. Their CCSD(T) potential curve had a well depth  $\sim 2.5\%$  too small. Results of similar accuracy have been obtained, using the CCSD(T) method and the aug-cc-pV5Z basis supplemented by a ( $3s3p2d2f1g$ ) set of bond functions, by Cybulski and Toczyłowski [53].

The most accurate *ab initio* argon–argon potential to date has been developed by Slavicek *et al.* [54]. These authors performed CCSD(T) calculations in bases up to aug-cc-pV6Z supplemented with a ( $3s3p2d2f1g$ ) set of midbond functions. Furthermore, they calculated the

core and core-valence correlation corrections (at the aug-cc-pV5Z+( $3s3p2d2f1g$ ) midbond level) and estimated the higher-level correlation contributions by performing full CCSDT calculations in a smaller basis set. These authors, however, did not use their large basis set results to extrapolate the interaction energy to the CBS limit. On the other hand, Jeziorska *et al.* [6] have recently shown that extrapolations from bases using bond functions greatly improve the predicted values of interaction energies. These extrapolations are more reliable than analogous extrapolations from bases without such functions. Therefore, it is worth investigating how the CBS extrapolation can improve the accuracy of the argon–argon potential obtained by Slavicek *et al.* [54].

In this work, the *ab initio* argon–argon potential developed by Slavicek *et al.* [54] has been refined in two ways. First, we extend the CCSD(T) calculations to intermonomer distances corresponding to the highly repulsive wall probed in the cross-section measurements analysed by Phelps *et al.* [13]. Next, we perform an extrapolation of the finite-basis-set results to the CBS limit. The extrapolated interaction energies are then fitted to an analytic formula which is an extension of the one developed by Korona *et al.* [5].

The structure of the rest of this paper is as follows. In section 2, key theoretical and computational aspects of obtaining an accurate argon–argon potential are discussed. The potential is presented and analysed in section 3. Section 4 discusses the spectra of  $\text{Ar}_2$  and section 5 analyses the virial coefficients. Finally, section 6 contains a brief summary of our work and perspectives for future work on the argon dimer potential.

## 2. Methodology and computational details

The interaction energies for 47 different argon–argon distances have been obtained from the supermolecular [55] CCSD(T) approach with the counterpoise scheme of Boys and Bernardi [56] to eliminate the basis set superposition error. For each point, results computed in three consecutive basis sets were used: the aug-cc-pVQZ, aug-cc-pV5Z and aug-cc-pV6Z bases supplemented by a ( $3s3p2d2f1g$ ) set of midbond functions (denoted as *spdfg* in Slavicek *et al.* [54]). These basis sets are the same as employed by Slavicek *et al.* [54], and for intermonomer distances greater than or equal to  $2 \text{ \AA}$ , we utilized the interaction energies calculated by these authors. For smaller distances, we calculated the energies ourselves, employing the same basis sets and the MOLPRO suite of codes [57]. When going to the intermonomer distances smaller than  $1 \text{ \AA}$ , the most diffuse midbond functions had to be successively

removed from the basis set to avoid linear dependencies. Exactly as in Slavicek *et al.* [54], the core and core-valence correlation correction has been established by performing calculations in the aug-cc-pV5Z + *spdfg* basis set with all electrons correlated. This quantity has not been extrapolated.

Following the approach employed by Murdachaew *et al.* [58], the finite-basis interaction energies were extrapolated to the CBS limit, using separate extrapolations for the SCF and correlation parts of the interaction energy:

$$E_{\text{int}}(\text{CBS}) = E_{\text{SCF}}(\text{CBS}) + E_{\text{corr}}(\text{CBS}). \quad (1)$$

The SCF energies have been observed to converge exponentially with  $n$  in a series of (aug)-cc-pVnZ basis sets [59], so we assumed that the SCF interaction energy calculated in the  $n$ -tuple zeta basis set behaves like

$$E_{\text{SCF}}(nZ) = E_{\text{SCF}}(\text{CBS}) + Ae^{-Bn}. \quad (2)$$

The CBS limit of the SCF interaction energy,  $E_{\text{SCF}}(\text{CBS})$ , can now be determined from the interaction energies calculated in three consecutive basis sets,  $(n-1)$ -,  $n$ -, and  $(n+1)$ -tuple zeta (in our case, these were the bases aug-cc-pVQZ + *spdfg*, aug-cc-pV5Z + *spdfg*, and aug-cc-pV6Z + *spdfg*, respectively), using the extrapolation formula

$$E_{\text{SCF}}(\text{CBS}) = \frac{E_{\text{SCF}}((n-1)Z)E_{\text{SCF}}((n+1)Z) - E_{\text{SCF}}^2(nZ)}{E_{\text{SCF}}((n-1)Z) + E_{\text{SCF}}((n+1)Z) - 2E_{\text{SCF}}(nZ)}. \quad (3)$$

The CBS-extrapolated values of the correlation part of the interaction energy  $E_{\text{corr}}(\text{CBS})$  were obtained using the calculated values from bases aug-cc-pV5Z + *spdfg* and aug-cc-pV6Z + *spdfg* and the so-called  $X^{-3}$  extrapolation scheme which assumes that the difference between the CBS energy and the energy calculated within an  $n$ -tuple zeta basis set vanishes like  $n^{-3}$  and leads to the following expression for the limit energy:

$$E_{\text{corr}}(\text{CBS}) = \frac{n_2^3 E_{\text{corr}}(n_2Z) - n_1^3 E_{\text{corr}}(n_1Z)}{n_2^3 - n_1^3}, \quad (4)$$

where, in our case,  $n_1 = 5$  and  $n_2 = 6$ . The above assumption is supported by theoretical investigations [60–62] as well as by a number of numerical studies, including ones concerning, as in this work, the interaction potentials of weakly bound systems [6, 63].

To obtain an analytic representation of the argon–argon potential, the calculated CCSD(T) interaction energies were fitted to a formula which is an extension

of the form proposed by Korona *et al.* [5],

$$V(R) = (A + A'R + A''/R)e^{-\alpha R + \beta R^2} - \sum_{n=3}^8 f_{2n}(bR) \frac{C_{2n}}{R^{2n}}, \quad (5)$$

where  $A, A', A'', \alpha, \beta$ , and  $b$  are fitting parameters,  $C_{2n}$  are the asymptotic constants and the Tang-Toennies damping functions  $f_{2n}(x)$  [64] are defined by

$$f_{2n}(x) = 1 - e^{-x} \sum_{k=0}^{2n} \frac{x^k}{k!}. \quad (6)$$

The role of the additional linear parameters  $A'$  and  $A''$ , not used in the helium dimer fit of Korona *et al.* [5], is to provide more flexibility in the highly repulsive region and, in the case of  $A''$ , to enable reproduction of the correct small- $R$  asymptotic behaviour of the interaction potential. The introduction of terms containing  $A'$  can also be expected to improve the medium-range behaviour of the potential since it is known from the work of Herring [65] that the exchange energy for a hydrogen atom interacting with a proton decays with  $R$  like  $cRe^{-dR}$ , just like our short-range term does.

An accurate value of the leading asymptotic constant  $C_6$  can be extracted from the experimentally measured differential oscillator strength distributions (DOSD) in the resonance absorption spectra of atoms [66] and has been recently obtained in this way by Kislyakov [67]. The result, equal to 64.691 a.u., with an estimated error of 0.04%, is in reasonably good agreement with several up-to-date *ab initio* results, including the value  $C_6 = 64.80$  a.u. obtained in a TDMP2 calculation by Hattig and Hess [68]. These authors also determined the values of  $C_8 = 1644$  a.u. and  $C_{10} = 50\,240$  a.u., which we employed in the fitting formula (5). The higher asymptotic constants  $C_{12} - C_{16}$  in equation (5) have been obtained from  $C_6, C_8$  and  $C_{10}$  using an extrapolation formula proposed by Thakkar [69]. The free parameters  $A, A', A'', \alpha, \beta$ , and  $b$  have been determined by a nonlinear least-squares fit with the 47 calculated points weighed proportionally to  $1/(E + 100 \text{ cm}^{-1})^2 \approx 1/(E - D_e)^2$ . A FORTRAN routine calculating the value of the fitted potential for a given distance  $R$  is available from the authors upon request.

It is worth mentioning that our form of the fit, equation (5), leads to unphysical values of the potential for distances  $\sim 0.1 \text{ \AA}$  smaller than the one for which the closest *ab initio* point was calculated. To avoid artifacts in applications of this potential, we have regularized it at short-range, i.e. replaced equation (5) for  $R < 0.15 \text{ \AA}$

by the simpler function

$$\tilde{V}(R) = \frac{\tilde{A}'' e^{-\tilde{\alpha}R}}{R}, \quad (7)$$

where the parameters  $\tilde{A}''$  and  $\tilde{\alpha}$  were determined such that the potential and its first derivative (evaluated analytically) agreed at  $R=0.15 \text{ \AA}$ .

### 3. Comparison with literature potentials

The performance of the CBS extrapolation from the results calculated in bases aug-cc-pVnZ + *spdfg*,  $n=4, 5, 6$ , is presented in table 1. From this table, it is clear that, although very large basis sets have been used in the calculations, the effect of the CBS extrapolation

still plays an important role in obtaining an accurate interaction potential. The estimated contribution to the CCSD(T) energy which is not recovered at the augmented sextuple zeta + midbond level amounts to  $-0.37 \text{ cm}^{-1}$  at the near van der Waals minimum distance  $R=3.775 \text{ \AA}$  and is larger for smaller  $R$ , being at least as important as the core and core-valence correlation correction at distances corresponding to the highly repulsive wall. In the region of the van der Waals minimum, both the CBS extrapolation and inclusion of the core correction are crucial for obtaining an interaction potential with accuracy better than  $1 \text{ cm}^{-1}$ . At  $R=3.775 \text{ \AA}$ , our most accurate value ( $-99.24 \text{ cm}^{-1}$ , the last column of table 1) is deeper by the extrapolation increment of  $-0.37 \text{ cm}^{-1}$  than that of Slavicek *et al.* [54] ( $-98.87 \text{ cm}^{-1}$ ). The depths of minima,  $D_e$ , given by the respective fits are  $99.27 \text{ cm}^{-1}$

Table 1. Calculated and extrapolated values of the  $\text{Ar}_2$  interaction potential. The interaction energies calculated in the basis sets aug-cc-pV5Z + *spdfg* and aug-cc-pV6Z + *spdfg*, and the energies extrapolated from the *ab initio* results using the approach outlined in section 2, are presented in the first three columns. The results in the last column include also the correction for the core and core-valence correlation effects. The distances are given in  $\text{\AA}$  and the energies are in  $\text{cm}^{-1}$ . The finite-basis energies and core corrections for distances equal to  $2 \text{ \AA}$  and larger have been calculated by Slavicek *et al.* [54].

$R$	aug-cc-pV5Z + <i>spdfg</i>	aug-cc-pV6Z + <i>spdfg</i>	Extrapolated	Extr. + core correction
0.25	34 888 652.5	34 143 824.7	33 600 680.7	33 597 120.2
0.4	11 644 214.9	11 490 997.2	11 430 211.1	11 428 838.0
0.6	3 980 529.1	3 944 966.1	3 932 158.2	3 926 926.7
0.8	1 775 126.6	1 765 636.8	1 761 466.7	1 757 165.1
1.0	794 074.0	788 472.2	784 435.9	782 122.9
1.2	384 699.9	382 465.0	381 013.4	379 771.6
1.4	229 369.6	228 244.1	227 386.8	226 650.2
1.6	129 322.0	128 740.1	128 236.0	127 764.6
1.8	70 174.7	69 900.1	69 631.6	69 341.6
2.0	36 539.5	36 409.5	36 270.3	36 100.4
2.4	8870.82	8836.80	8795.77	8737.45
2.8	1766.00	1756.24	1743.77	1724.79
3.2	182.660	180.088	176.701	170.353
3.4	-16.7911	-18.0249	-19.6695	-23.4522
3.6	-84.8214	-85.4064	-86.1903	-88.4975
3.7	-95.0284	-95.4190	-95.9367	-97.7956
3.75	-96.7432	-97.0583	-97.4753	-99.1808
3.775	-96.9650	-97.2438	-97.6135	-99.2385
3.8	-96.8495	-97.1011	-97.4316	-98.9903
3.9	-93.6635	-93.8176	-94.0179	-95.3420
4.0	-87.6799	-87.7390	-87.8150	-88.9182
4.2	-72.5886	-72.5721	-72.5464	-73.3182
4.4	-57.6674	-57.6299	-57.5824	-58.0941
4.6	-44.9594	-44.9275	-44.8838	-45.1881
5.0	-26.9818	-26.9589	-26.9246	-27.0832
6.0	-8.2861	-8.2817	-8.2797	-8.3406
7.0	-3.0771	-3.0760	-3.0744	-3.1069
8.0	-1.3249	-1.3249	-1.3249	-1.3348
10.0	-0.3318	-0.3319	-0.3320	-0.3333
14.0	-0.0425	-0.0424	-0.0422	-0.0424
20.0	-0.0049	-0.0049	-0.0049	-0.0050

and  $98.93\text{ cm}^{-1}$ , a difference of  $0.34\text{ cm}^{-1}$ . Notice that table I of Slavicek *et al.* [54] gives  $98.8\text{ cm}^{-1}$  as  $D_e$  for the level of theory discussed here, apparently due to some roundoff error.

The well depth of our potential ( $99.27\text{ cm}^{-1}$  fit value) differs from the depth of the empirical Aziz [10] potential, equal to  $99.55\text{ cm}^{-1}$ , by just  $0.28\text{ cm}^{-1}$  or 0.3%. It is worth noting that performing the CBS extrapolation results in cutting the difference between the Aziz result and the non-extrapolated value in half. Our depth agrees even better with the value extracted from the spectroscopic measurements of Herman *et al.* [70], equal to  $99.2 \pm 1.0\text{ cm}^{-1}$ . One should also mention here an older experimental well depth based on the spectra measured by Colbourn and Douglas [71] equal to  $99.55\text{ cm}^{-1}$  (no error bars given). This is actually more an empirical than experimental result, as in addition to spectral data the authors used information from virial measurements and theoretical  $C_n$  constants to obtain this value.

For a further increase of the accuracy of the *ab initio* potential, the correlation effects beyond CCSD(T) have to be included. One may note that a partial inclusion of these effects by Slavicek *et al.* [54]—utilizing the full CCSDT calculation carried out in a much smaller basis set than those used in the CCSD(T) calculations—actually worsened the agreement of their potential with the Aziz [10] potential, and the agreement of the resulting rovibrational spectra with the experimental results. This fact suggests that the effects of higher-than-triple excitations may be, as could be expected on theoretical grounds, of comparable size as the contribution CCSDT-CCSD(T). We could not include the complete triples correction in our potential since it has apparently been computed by Slavicek *et al.* [54] only at four values of  $R$ , not enough for high-accuracy fitting in the broader range of  $R$  used in our work.

The parameters defining our analytical fit to the set of CBS-extrapolated CCSD(T) interaction energies, with the core correction included (i.e. to the data in the last column of table 1), are gathered in table 2. The accuracy of our fit around the van der Waals minimum is close to 0.01% (the depth of the fit being equal to  $99.27\text{ cm}^{-1}$ ) and it worsens to slightly below 0.2% for distances around  $4.2\text{ \AA}$ . This behaviour of the fit can be attributed mainly to the fact that the leading constant  $C_6$ , governing the asymptotics of the fitted potential, is nearly exact and was *not* calculated from our CCSD(T) interaction energies. Due to the improved asymptotic behaviour, our analytical fit may be viewed as an even more reliable description of the Ar-Ar potential for large distances than our extrapolated *ab initio* points. In fact, in the asymptotic region our potential is certainly more accurate than the commonly used HFDID1

potential of Aziz [10], since the latter employs a significantly underestimated value of  $C_6 = 63.50\text{ a.u.}$ ; note that the earlier potentials of Aziz and Slaman [14] used the value of  $C_6 = 64.30\text{ a.u.}$  obtained by Kumar and Meath [66], closer to the most accurate available value of  $64.691\text{ a.u.}$  [67].

### 3.1. Van der Waals minimum region

The behaviour of our calculated and fitted argon–argon potential at the van der Waals minimum region is graphically displayed in figure 1. For comparison, we have also drawn the curves corresponding to the Aziz [10] HFDID1 potential and the potential fitted by Slavicek *et al.* [54] to their non-extrapolated, core-corrected aug-cc-pV6Z + *spdfg* results. As is explained in section 4, the fit of Slavicek *et al.* (with the parameters given in table 8 of [54]), presented in figure 1, does *not* include the CCSDT-CCSD(T) correction. It is clearly seen that these three currently most accurate argon–argon potentials have reached an unprecedented level of consistency. As discussed in the previous paragraph, for distances larger than the minimum, our potential is slightly deeper than the Aziz potential since it employs a larger, more accurate value of the asymptotic constant  $C_6$ . For distances smaller than the minimum, the Aziz potential becomes progressively deeper than ours as  $R$  decreases, up to a few inverse centimetres at the smallest  $R$  in figure 1, which means it has a softer wall than both the *ab initio* potentials.

Table 2. Parameters of our analytical fit of the calculated argon–argon interaction energies to the formula (5), expressed in atomic units of energy and length. Not all presented digits are significant. Note that the values of the asymptotic constants  $C_n$  were *not* fitted.

Parameter	
A	−134.209 907 5
A′	62.932 592 2
A″	206.875 820 2
$\alpha$	1.623 806 026
$\beta$	−0.046 730 112 7
$b$	1.500 497 187
$C_6$	64.691 <sup>a</sup>
$C_8$	1644 <sup>b</sup>
$C_{10}$	50 240 <sup>b</sup>
$C_{12}$	1 898 195 <sup>c</sup>
$C_{14}$	86 445 426 <sup>c</sup>
$C_{16}$	4 619 452 502 <sup>c</sup>
$\tilde{A}''$	32 837.873 43
$\tilde{\alpha}$	19.772 617 9

<sup>a</sup>[67].

<sup>b</sup>[68].

<sup>c</sup>Extrapolated from  $C_6$ – $C_{10}$  using the scheme of Thakkar [69].

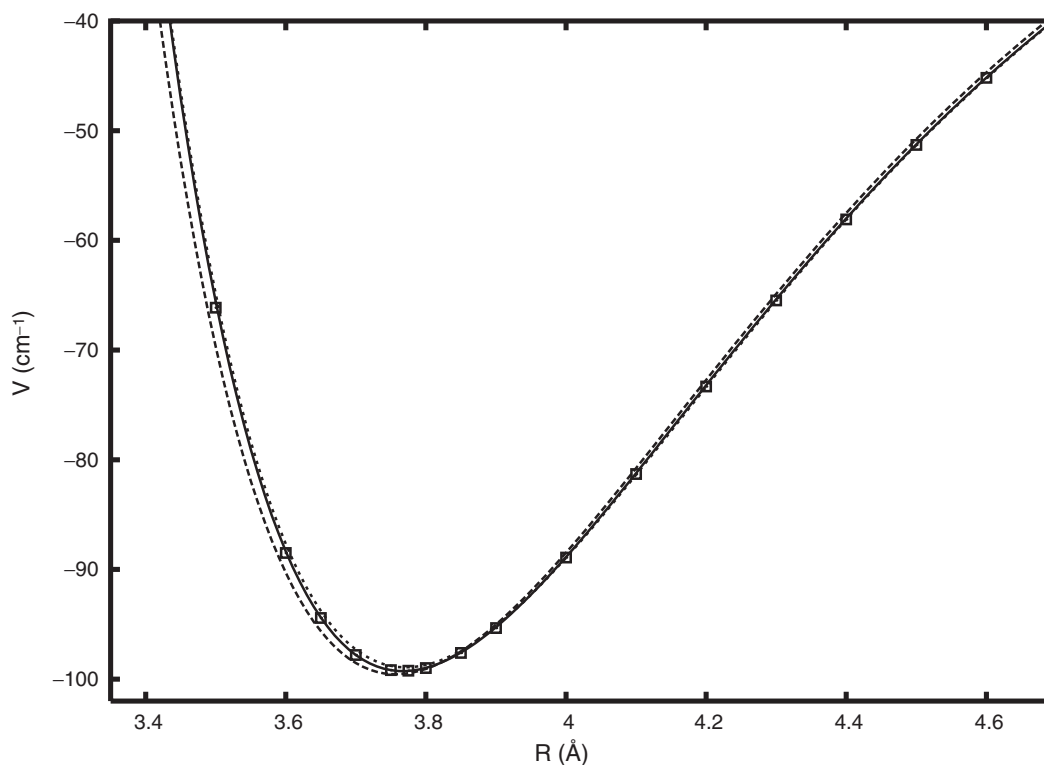


Figure 1. The van der Waals minimum region of the argon–argon interaction. Our extrapolated single-point energies are denoted by squares, and the solid line represents our analytical fit to these points (table 2). The long-dashed line represents the Aziz [10] empirical potential and the short-dashed line is the potential fitted by Slavicek *et al.* [54] (table 8).

### 3.2. Highly repulsive region

At distances corresponding to the highly repulsive wall of the argon–argon potential, the differences between various potentials available are much more significant. The behaviour of our potential and of several others in this region has been presented in figure 2. For these distances, the agreement between our calculated and fitted results was, of course, not as good as for larger  $R$ —the differences between the above quantities amounted to  $\sim 3\%$  on the average and up to 10% for some points (this is partly due to the weights used in our fitting procedure). Nevertheless, as figure 2 shows, the discrepancies between various potentials are significantly larger than inaccuracies of the fit.

The work of Aziz and Slaman [14] was aimed at improving the representation of the argon dimer potential in the region of  $R$  in the range 1.7–2.7 Å, corresponding to energies in the range of  $\sim 0.5$ –10 eV or 3000–100 000  $\text{cm}^{-1}$ , where actual numerical values of the potential are known from the inversion of beam scattering data of Rol [72]. The experimental data are shown in figure 3 together with the most recent empirical potentials of Aziz–Slaman [14] and Aziz [10]. The HFD-B3 potential has a single functional form

and fits the points obtained by Rol [72] to within experimental error bars. However, this potential did not reproduce the available high-temperature viscosity and thermal conductivity data satisfactorily enough [14]. Therefore, Aziz and Slaman [14] proposed another potential, a piece-wise one denoted by HFDTCS2, which was equal to HFD-B3 down to  $R = 2.98$  Å and then was joined by a spline to a simple exponential starting at  $R = 2.73$  Å. This exponential was chosen such that HFDTCS2 passes near the upper end of the experimental range, see figure 3. Although HFDTCS2 represented the Rol [72] data a little worse than HFD-B3, it recovered the other data mentioned above much better and this potential was the one recommended by Aziz and Slaman. Figure 3 displays also the HFDID1 potential of Aziz [10] which was fitted to Rol [72] data but otherwise was aimed at reproducing low-temperature experiments. In fact, high-temperature properties have not been computed for this potential. The Phelps *et al.* [13] potential, which will be discussed in more detail below, is also shown in figure 3. For  $R > 2.65$  Å (5 bohr), this potential is equal to HFD-B3 and for the remainder of the  $R$  range shown it is a spline joining HFD-B3 to the higher-energy region. Clearly, the Phelps *et al.*

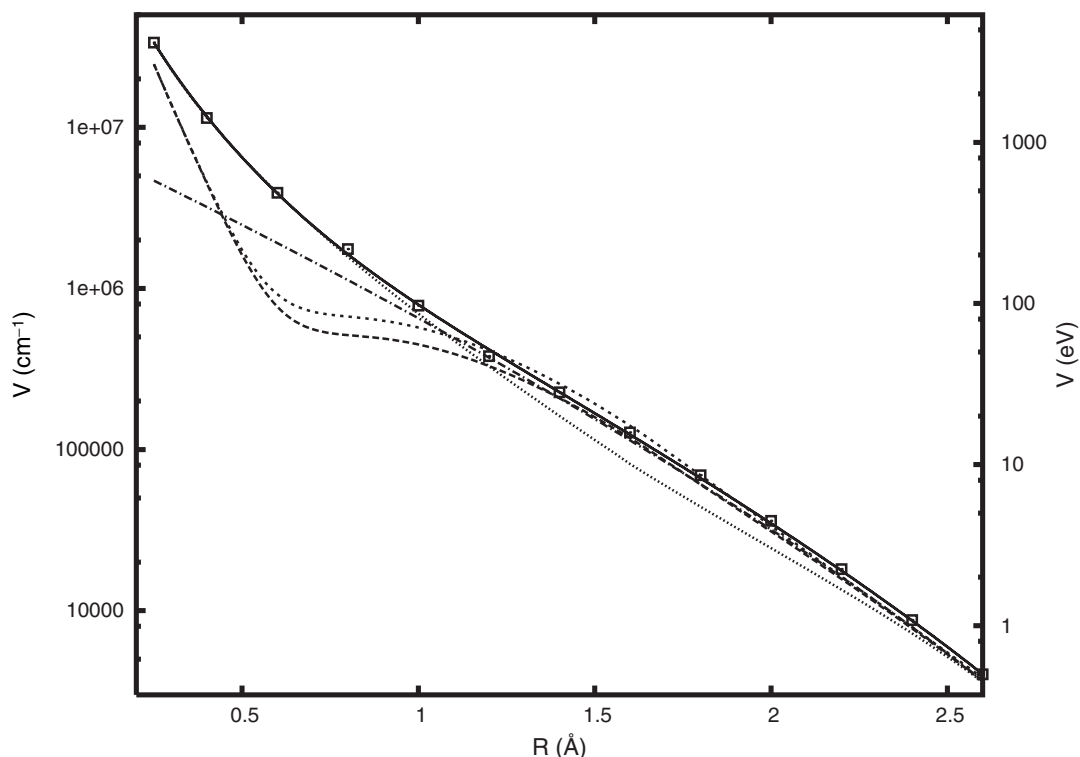


Figure 2. The highly repulsive wall of the argon–argon interaction. Our extrapolated single-point energies are denoted by squares and the solid line represents our analytical fit to these points (table 2). The long-dashed line represents the Aziz and Slaman [14] empirical HFD-B3 potential and the short-dashed line shows the short-range part of the piecewise-constructed potential HFDTC S2 from the same paper. The dash-dotted line is the more recent, 1993 potential of Aziz [10] and the dotted line represents the empirical potential recommended by Phelps *et al.* [13] on the basis of fitting several high-energy cross-section measurements. Note the logarithmic scale on the vertical axis.

[13] potential does not reproduce Rol [72] data well for  $R$  smaller than  $2 \text{ \AA}$ .

Figure 3 shows that our potential falls within experimental error bars for smaller and larger  $R$  and is up to about one deviation from the upper experimental range in the middle. The deviations of the present potential from the empirical potentials are similar in magnitude to the differences between the empirical potentials. With this behaviour, our potential may do very well in predicting high-temperature measurements. Notice also that the behaviour of all the potentials included in figure 3 may indicate some systematic downward shift of the experimental data in the middle of the displayed  $R$  range.

The very-high energy region of the potential is shown in figure 2. Aziz and Slaman considered their potentials to be determined by the available data only down to an  $R$  of  $1.7 \text{ \AA}$ , the lowest  $R$  in the Rol [72] data. They recommended that for smaller  $R$  the potential should be represented by the united atom theoretical potential of Pathak and Thakkar [73], with the region  $0.2 \text{ \AA} < R < 1.7 \text{ \AA}$  interpolated by a spline. The unusual behaviour of the Aziz-Slaman potentials seen in figure 2

is just an artifact of the spline interpolation. The HFDID1 potential of Aziz [10] was not extended in such a way, so that figure 2 shows just the values computed from the overall formula.

The high-energy region of the Phelps *et al.* [13] potential,  $R$  smaller than  $1.6 \text{ \AA}$  (3 bohr), is taken from a fit done by the authors to the Kim-Gordon electron gas calculations by Gianturco and Dilonardo [74] based on accurate SCF atomic densities. The potential of Phelps *et al.* [13] gave reasonable predictions for several experiments sensitive to the very high-energy region [15–17]. Despite some deviations visible in figure 3, it gave also good predictions in the mildly repulsive region, i.e. for collision energies smaller than  $10 \text{ eV}$ . Apparently, the energies where the deviations are large are not particularly important for these experiments and the fact that Phelps *et al.* potential becomes equal to the HFD-B3 potential starting at  $R > 5 \text{ bohr}$  ( $V < 1 \text{ eV}$ ) is sufficient to assure accurate predictions.

As it is clearly seen in figure 2, the potential developed by us agrees extremely well with the potential of Phelps *et al.* [13] for energies larger than  $100 \text{ eV}$ .



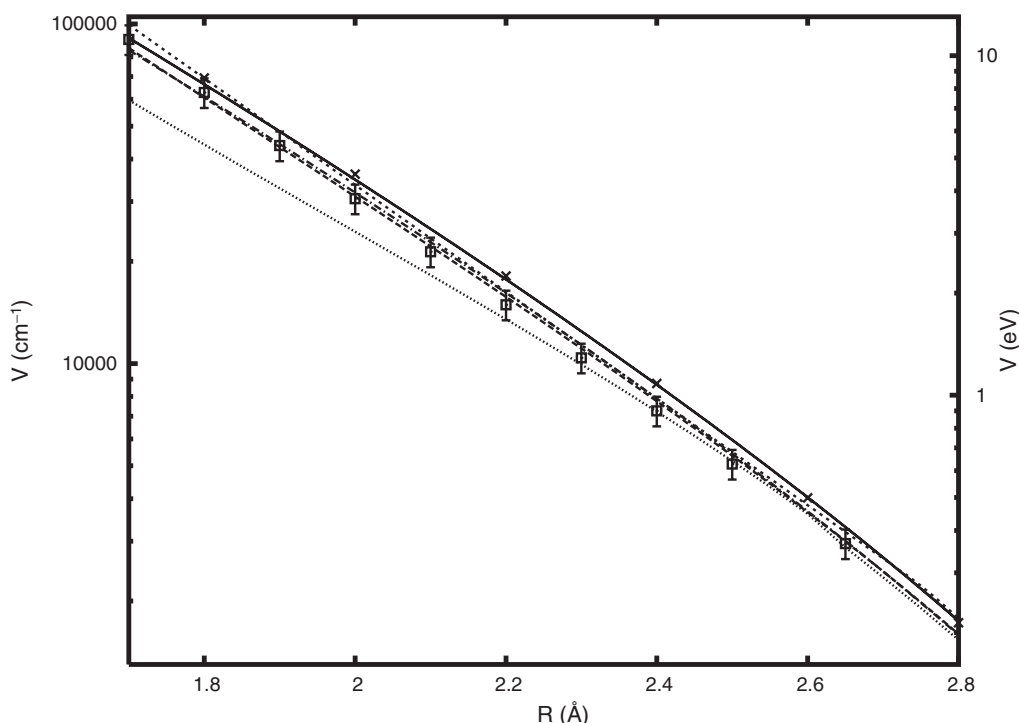


Figure 3. The mildly repulsive region of the argon–argon interaction. The solid line represents our fitted potential (our computed points, denoted by ‘x’, are also shown), the long-dashed line is the Aziz and Slaman [14] empirical HFD-B3 potential and the short-dashed line shows the piecewise-constructed potential HFDTCS2 from the same paper. The dash-dotted line is the more recent, 1993 potential of Aziz [10] and the dotted line represents the empirical potential recommended by Phelps *et al.* [13] on the basis of fitting several high-energy cross-section measurements. The squares denote the experimental beam potential data of Rol [72]. The experimental error bars are also given. Note the logarithmic scale on the vertical axis.

Comparison of figures 2 and 3 suggests that our potential is probably the best representation of the true potential in the range 10–100 eV. Since, as discussed above, this potential is also comparable in accuracy to empirical potentials in the range 1–10 eV, it is clearly the best overall representation for the whole high-energy range of 1–10 000 eV.

The agreement of our potential with the values computed by Gianturco and Dilonardo [74] is perhaps surprisingly good taking into account that these authors have used a fairly approximate theoretical method. However, for very small  $R$  (in contrast to the negative energy region), the potential becomes in fact very well described by simple methods. For example, for  $R=0.6$  Å, the Hartree-Fock method gives the interaction energy with only 4% error. At  $R=0.5$  and 1.0 bohr, Gianturco and Dilonardo’s interaction energies differ from those given by our potential by only 1% and 0.2%, respectively. Such small differences are hardly visible on a logarithmic scale.

One may also note that the Aziz-Slaman [14] or Aziz [10] potentials shown in figure 2 would clearly give poor results in predicting quantities depending on the very-high-energy region, as these are several times lower

than the potential of Phelps *et al.* [13] or our potential. One may note that if the HDF-B3 and HFDTCS2 potentials were not connected to the united atom potential as described above, these would behave somewhat better (but they still would be far from our potential) in the range 0.5–1 Å. Only for  $R$  smaller than  $\sim 0.3$  Å does the interpolated model become more accurate.

#### 4. Spectra of argon dimer

The characteristic properties of the potential: the position  $R_e$  and depth  $D_e$  of the van der Waals minimum, as well as the dissociation energy  $D_0$  and the rotational constant  $B_0$ , are gathered in table 3. For comparison, we included also the characteristic properties of several other argon–argon potentials [10, 14, 52–54, 75], as well as the values measured by Herman *et al.* [70]. The one-dimensional Schrödinger equation for the relative motion of the argon nuclei was solved numerically, employing the finite difference method implemented in terms of a tri-diagonal matrix, as described by Cooney *et al.* [76]. The finite-difference

Table 3. Characteristic properties of the argon dimer predicted by various potentials.

Property	This work	[53]	[52]	[54]	HFDID1 [10]	HFD-B3 [14]	Experiment [70]
$R_e$ (bohr)	7.119	7.140	7.139	7.126	7.100	7.107	7.107 (6)
$D_e$ (cm <sup>-1</sup> )	99.27	96.99	97.60	98.93 <sup>a</sup>	99.55	99.56	99.2 (10)
$D_0$ (cm <sup>-1</sup> )	84.38	82.38	82.98	84.16	84.75 <sup>b</sup>	84.71 <sup>c</sup>	84.47 (10) <sup>d</sup>
$B_0$ (cm <sup>-1</sup> )	0.05743 <sup>e</sup>	0.05708		0.05745	0.05777	0.05764 <sup>f</sup>	0.05776 (6)

<sup>a</sup>Value from fit *C*. Computed  $D_e$  at  $R = 3.775 \text{ \AA}$  is  $98.87 \text{ cm}^{-1}$ .

<sup>b</sup>Computed in the present work.

<sup>c</sup>From table 4 of Aziz *et al.* [75]. The value computed by us is  $84.66 \text{ cm}^{-1}$ .

<sup>d</sup>Experimental  $D_0$  minus  $G_0$  from table V of Herman *et al.* [70].

<sup>e</sup>Computed as half of the difference between  $J = 1$  and 0 levels.

<sup>f</sup>Computed by Aziz [10].

Table 4. Energy differences (in cm<sup>-1</sup>) between consecutive vibrational levels with rotational quantum number  $J = 0$  of the argon dimer, predicted by several different potentials and compared to the measured values.

$v' - v''$	This work	[54] <sup>a</sup>	HFDID1 [10]	HFD-B3 [14] <sup>b</sup>	Experiment [70]
1 – 0	25.75	25.58	25.68	25.75	25.69 (1)
2 – 1	20.48	20.44	20.56	20.51	20.58 (2)
3 – 2	15.44	15.46	15.58	15.51	15.58 (2)
4 – 3	10.79	10.78	10.92	10.87	10.91 (3)
5 – 4	6.76	6.74	6.83	6.81	6.84 (7)

<sup>a</sup>Quoted from Slavicek *et al.* [54]. Our calculations give values up to  $0.06 \text{ cm}^{-1}$  different.

<sup>b</sup>Computed by Aziz [10]. Notice that values quoted in table 4 of Aziz *et al.* [75] are slightly different.

solutions were then extrapolated to zero step size by means of a Richardson extrapolation [77]. For the argon–argon potentials available in the literature, the rovibrational levels calculated by the above method agreed with their respective literature values to within  $0.02 \text{ cm}^{-1}$  (mostly to within  $0.01 \text{ cm}^{-1}$ ). The only exception are the results of Slavicek *et al.* [54], where the discrepancies were up to  $0.06 \text{ cm}^{-1}$ .

The characteristic properties of the argon–argon potentials listed in table 3 confirm that the state-of-the-art *ab initio* (this work and Slavicek *et al.* [54]) and empirical (Aziz [10]) potentials are very close to each other and must be very close to the true interaction potential probed in experiments. Note that the values given for the Slavicek *et al.* potential correspond to their analytic fit with the parameters specified in table 8 of [54]. This fit apparently corresponds to the data marked ‘*C*’ in tables 10–13 of Slavicek *et al.* [54], i.e. the CCSDT-CCSD(T) correction was *not* included. As already mentioned, adding this correction (cf. the columns marked ‘*CC*’ in tables 10–13 of Slavicek *et al.* [54]) actually worsened the agreement with experiment for all quantities compared and we have not included these results in the tables. The slightly older potentials of Fernandez and Koch [52] and Cybulski and Toczyłowski [53] give noticeably less accurate results

for all the quantities listed. Comparing to the potential of Slavicek *et al.* [54], one may note that the CBS extrapolation and a different fitting procedure employed by us lead to a significantly better agreement with experiment for the dissociation energy  $D_0$ . It did not, however, influence the value of the rotational constant which remained outside of the experimental error bars (see, however, a further discussion below).

Further assessment of the accuracy of various argon–argon potentials can be done by comparing the spacings between the lowest pure vibrational ( $J = 0$ ) levels, presented in table 4. As already observed by Slavicek *et al.* [54], the rovibrational spectra predicted by the potentials of Fernandez and Koch [52] and Cybulski and Toczyłowski [53] are not as accurate as the results obtained from newer potentials, so we excluded those potentials from further comparisons. As can be seen from table 4, in the case of vibrational spacings, in contrast to  $D_e$  and  $D_0$ , our results do not agree significantly better with experiment than the ones predicted by the Slavicek *et al.* potential (the data marked ‘*C*’ in table 11 of Slavicek *et al.* [54]): out of five quanta, our predictions are slightly closer to experiment in four cases. One may say that both sets are almost equally distant from experiment. This is not surprising, since a fairly uniform shift of the

potential should have a small effect on vibrational quanta.

Our vibrational quanta generally agree with the experimental results of Herman *et al.* [70] to  $\sim 0.1 \text{ cm}^{-1}$ . For the 5–4 transition, the discrepancy of  $0.08 \text{ cm}^{-1}$  is very close to the experimental error bar of  $0.07 \text{ cm}^{-1}$ . For the remaining transitions, however, the experimental error bars are smaller,  $0.01\text{--}0.03 \text{ cm}^{-1}$ , and, therefore, our predictions are several standard deviations outside the experimental range. The agreement in absolute terms is similar to that achieved for  $D_e$  and  $D_0$ , but now the experimental uncertainties are much smaller. The empirical Aziz potential [10] was fitted to the experimental rovibrational quanta and obviously gives results within experimental error bars.

The experimental values of  $R_e$ ,  $D_e$  and  $D_0$  listed in table 3 result from a fairly involved processing of measured data. It is also worth mentioning, however, that the rotational constants and vibrational quanta listed in tables 3 and 4 are not directly measured in rovibronic experiments and there exists some small arbitrariness in obtaining these quantities. In fact, Boyes [12] reanalysed the data of Herman *et al.* [70] and obtained somewhat different results. For example, the rotational constant recommended by Boyes is  $0.057\,55 \pm 0.000\,11 \text{ cm}^{-1}$ , which differs by  $0.000\,21 \text{ cm}^{-1}$  from the value published by Herman *et al.* [70] and agrees with our value almost to within experimental error bars. The vibrational quanta obtained by Boyes are  $0.01\text{--}0.04 \text{ cm}^{-1}$  different from those originally published. In three out of five cases, our results agree better with the former than with the latter data. On the other hand,

Aziz's [10] potential predictions are outside Boyes' error bars in two cases.

We have also included in tables 3 and 4 the results obtained with the HFD-B3 potential of Aziz and Slaman [14]. This potential was apparently considered by Aziz to be the best of several potentials developed by him, as he recommended it in a 1996 review [75]. The HFD-B3 potential was fitted to the older spectroscopic data of Colbourn and Douglas [71], so it does not agree as well with the Herman *et al.* [70] quanta as HFDID1 does [10]. Table 4 shows that the vibrational quanta obtained from our potential agree significantly better with those produced by HFD-B3 than by HFDID1, but this is probably accidental.

## 5. Virial coefficients

The second virial coefficients,  $B(T)$ , are important quantities to compare two-body potentials with experiments since these quantities are by definition dependent only on two-body interactions. Moreover, due to the importance of the virial equation of state in thermal physics, extensive experimental data exist for most pure substances and many mixtures. Table 5 compares the second virial coefficients calculated with and without quantum corrections using the potential obtained in this work to those calculated using the *ab initio* potential of Slavicek *et al.* [54], the empirical potential of Aziz [10] and to experimental data [78]. One should mention here that Aziz did not use virial coefficients in the set of data that his potential was fitted to.

Table 5. Comparison of second virial coefficients  $B(T)$  obtained from various argon dimer potentials to experimental data. The values of  $B(T)$  were computed from the respective potentials by us using the classical expression ( $B_c$ ) and including a quantum correction ( $B_{c+q}$ ). Temperatures  $T$  are in K, virial coefficients and uncertainties are in  $\text{cm}^3 \text{ mol}^{-1}$ .

$T$	This work		Slavicek <i>et al.</i> [54]		Aziz [10]		Experiment [78]
	$B_c$	$B_{c+q}$	$B_c$	$B_{c+q}$	$B_c$	$B_{c+q}$	$B_{\text{exp}}$
100.00	-183.33	-181.84	-183.08	-181.61	-183.44	-181.98	-183.5 (10)
133.15	-108.12	-107.44	-108.02	-107.34	-108.26	-107.59	-109.2 (10)
150.00	-86.32	-85.81	-86.25	-85.75	-86.49	-85.99	-86.2 (10)
200.00	-47.89	-47.63	-47.87	-47.61	-48.15	-47.89	-47.4 (10)
250.00	-27.54	-27.37	-27.54	-27.37	-27.86	-27.70	-27.9 (10)
300.00	-15.04	-14.92	-15.06	-14.94	-15.41	-15.30	-15.5 (5)
400.00	-0.67	-0.60	-0.70	-0.62	-1.10	-1.03	-1.0 (5)
500.00	7.21	7.26	7.18	7.23	6.74	6.78	7.0 (5)
600.00	12.09	12.13	12.05	12.09	11.59	11.62	12.0 (5)
700.00	15.34	15.37	15.31	15.34	14.82	14.85	15.0 (10)
800.00	17.63	17.66	17.60	17.62	17.09	17.12	17.7 (10)
900.00	19.30	19.32	19.26	19.28	18.75	18.77	20.0 (10)
1000.00	20.54	20.56	20.51	20.53	19.99	20.00	22.0 (10)
1073.16	21.26	21.28	21.23	21.25	20.70	20.72	
1223.16	22.38	22.39	22.35	22.36	21.81	21.82	

The low-temperature virial coefficients calculated with the *ab initio* potentials of Fernandez and Koch [52] and Cybulski and Toczyłowski [53] had relatively larger positive deviations from experiment and are not shown. The coefficients computed by us from the Aziz's potential agree with analogous coefficients computed by Mas *et al.* [3] except for  $T = 133.15$  K for which there is a misprint in Mas *et al.* [3].

The quantum correction has been computed in the  $\hbar^2$  approximation. This approximation is completely sufficient for argon, as shown by Dardi and Dahler [79]. At the smallest temperature considered,  $T = 100$  K, the correction of the order of  $\hbar^2$  computed by Dardi and Dahler from the Koide *et al.* [80] potential is equal to  $1.49 \text{ cm}^3 \text{ mol}^{-1}$  (Aziz's [10] potential and our potential give  $1.47$  and  $1.49 \text{ cm}^3 \text{ mol}^{-1}$ , respectively, cf. table 5), whereas the full quantum correction is  $1.53 \text{ cm}^3 \text{ mol}^{-1}$ . The difference of  $0.04 \text{ cm}^3 \text{ mol}^{-1}$  is much smaller than current experimental error bars. As the results in table 5 show, the quantum corrections are completely negligible for temperatures larger than  $\sim 300$  K and are significant compared to experimental error bars only at the two lowest temperatures listed.

The theoretical results are compared to experiment [78, 81–84] in figure 4(a) and (b). Some experimental points have been taken from interpolations performed by Mas *et al.* [3]. The coefficients computed from the Slavicek *et al.* [54] potential are not shown since these would be indistinguishable from the coefficients computed with our potential except for  $T = 100$  K where, as shown in table 5, the former results would be  $0.22 \text{ cm}^3 \text{ mol}^{-1}$  further from experiment. The figures show deviations of computed values from reference experimental results. Notice that such a presentation strongly emphasizes the discrepancies. On a straightforward plot of  $B(T)$  vs  $T$ , all the discussed potentials would give results appearing to be in essentially perfect agreement with each other and with experiment.

Figure 4(a) displays the deviations from the values recommended by Dymond and Smith [78], who compiled experimental data from several sources. Such a choice was made since these recommendations are utilized by the CRC Handbook [85], a very popular reference source. Figure 4(a) and (b) shows both the classical coefficients and the ones with the quantum correction included. This confirms visually the statement made above about the quantum correction being important only for the two lowest temperatures from table 5. For these two temperatures, the quantum corrections do make a significant difference in comparisons to experimental data. From now on we will always refer exclusively to theoretical results with quantum corrections.

As it can be seen in figure 4(a) and in table 5, the virial coefficients predicted by our and Aziz's potentials agree very well. The latter values are fairly uniformly shifted down by  $\sim 0.6 \text{ cm}^3 \text{ mol}^{-1}$  at large  $T$  and by  $0.14 \text{ cm}^3 \text{ mol}^{-1}$  at the lowest  $T$ , the differences being smaller than the experimental error bars. Both sets of data lie within the experimental error bars from Dymond and Smith [78] for most of the range: from 150 to 900 K (800 K for Aziz's potential values). For high  $T$ , the virial coefficients are sensitive to the repulsive wall of the potential and the larger values obtained from our potential compared to that of Aziz are consistent with the softer wall in the latter case. For small  $T$ , where the virial coefficients are sensitive to the volume of the potential well, the two sets of coefficients are virtually identical, showing that the small differences in region of the van der Waals well visible in figure 1 are inconsequential for virial coefficients. From comparisons of the convergence of *ab initio* calculations and estimates of terms neglected by theory, it is clear that the exact potential cannot lie more than  $\sim 1 \text{ cm}^{-1}$  from our potential at the minimum. Therefore, the exact virial coefficient at low  $T$  should be very close to the current theoretical predictions and the discrepancies with the values recommended by Dymond and Smith [78] are hard to explain.

To understand the issue of agreement with experiment better, we have included several sets of experimental data in figure 4(a) and (b). First, for high temperatures, the values measured by Lecocq [84] (denoted by L-3 in figure 4(a)) are outside the errors bars of Dymond and Smith [78] and agree very well with theory in the range 800–1000 K. Thus, it is likely that theoretical values may better represent the exact virial coefficients than the values from Dymond and Smith [78].

For low  $T$ , one can clearly see that the experimental data from [81–83] follow the theoretical curve as it deviates from the recommendation of Dymond and Smith [78]. Thus, again theory may be more accurate than values of Dymond and Smith [78] at low temperatures. Figure 4(b) shows the expanded range of  $T$  from 133 to 400 K. In view of the observations made using figure 4(a), we have changed the reference point and used the data of Michels *et al.* [81] instead of those from Dymond and Smith [78]. Compared to the former data, the virial coefficients computed from Aziz's potential are within experimental error bars (notice that these are smaller than those of Dymond and Smith [78]) except for the two lowest points. Our potential predicts virial coefficients that are up to one standard deviation above the experimental range. However, the data from Gilgen *et al.* [82] and Tegeler *et al.* [83] are also at most points above the values of Michels *et al.* [81] and our results are within or very close to the upper range of the error bars of these measurements.

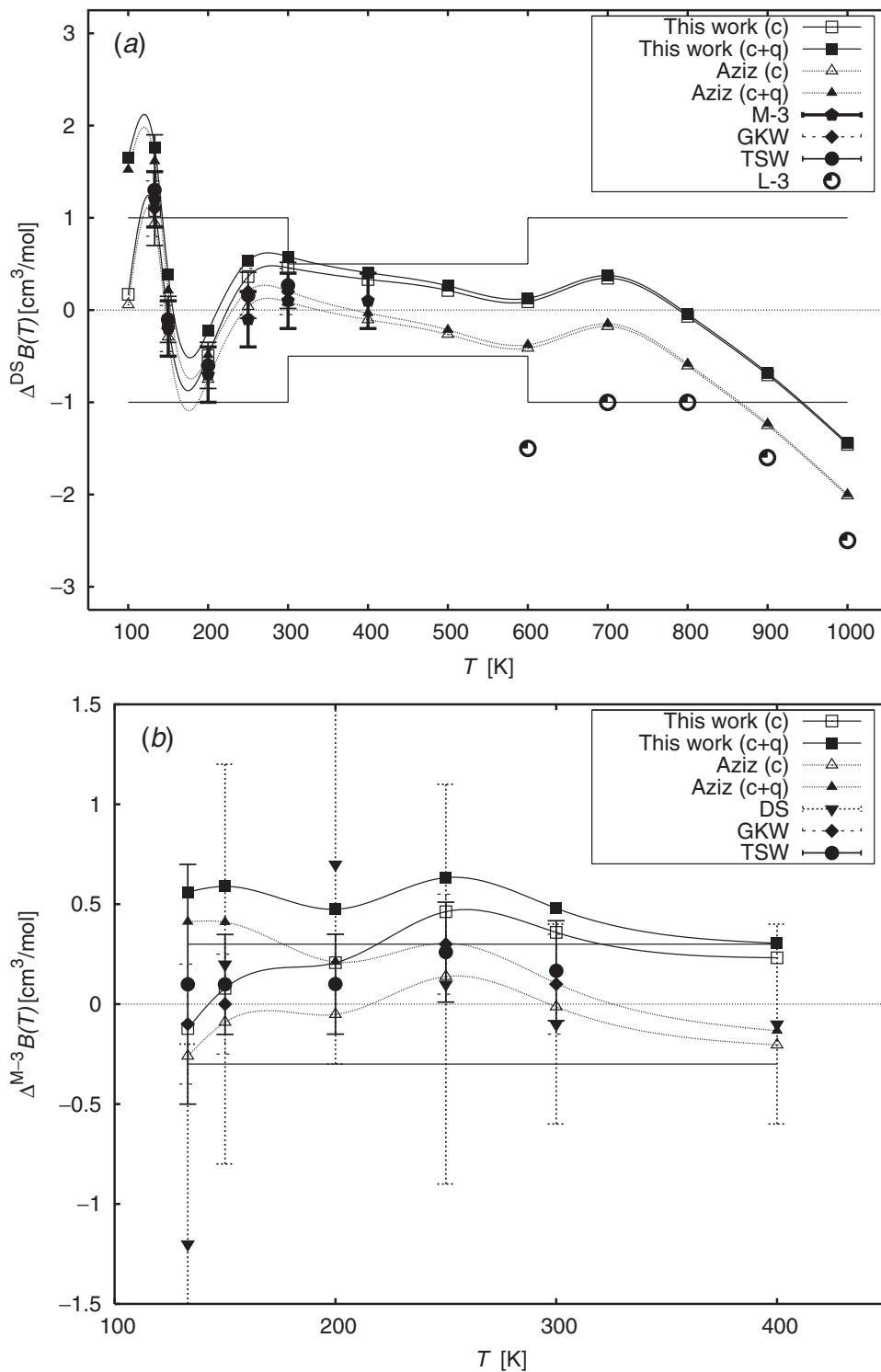


Figure 4. (a) Deviations of various second virial coefficients from values recommended by Dymond and Smith [78]. The theoretical coefficients calculated using our potential and the potential of Aziz [10] are shown as open symbols for the classical (c) and by filled symbols for the quantum (c+q) calculations. The lines connecting these symbols are drawn only to guide the eye. The light horizontal lines are the estimated uncertainties in the recommended values taken from Dymond and Smith [78]. The other experimental data included are from [81] (M-3), [82] (GKW), [83] (TSW) and [84] (L-3). The values used were taken from interpolations performed by Mas *et al.* [3] for the data of [81, 82, 84] and by us for the data of [83]. (b) Similar to (a), except that the reference data are those of Michels *et al.* [81]. The values recommended by Dymond and Smith [78] are denoted by DS.

Based on the present results, it appears that the compilation of Dymond and Smith [78] should not be used anymore as the standard reference for the second virial coefficients of argon. For temperatures larger than 300 K, the virials computed from either our potential or Aziz's potential appear to represent a more trustworthy reference point. For  $120\text{ K} < T < 340\text{ K}$ , the data of Tegeler *et al.* [83] appear to be the most accurate, also based on the agreement with theory. For  $T$  smaller than 120 K, again the theoretical data are probably the most accurate reference.

## 6. Conclusions

The present work developed a new *ab initio* potential for the argon dimer. This potential is based on CCSD(T) calculations in a sequence of aug-cc-pVnZ + *spd*fg basis sets,  $n = 4, 5, 6$  and CBS extrapolations. Our potential is an improvement of that developed recently by Slavicek *et al.* [54] who used the same basis sets, but did not apply CBS extrapolations. We have also computed points for  $R$  from 0.25 to 1.8 Å, which were not included in Slavicek *et al.* [54], and used a different functional form for the fit. At the van der Waals minimum, our potential is  $0.34\text{ cm}^{-1}$  deeper than that of Slavicek *et al.* [54], bringing the theoretical depth of the potential closer to the experimental value: the well depths obtained by Slavicek *et al.* [54], the present work and experiment [70] are 98.93, 99.27 (from the fit, the computed value at  $R = 3.775\text{ Å}$  is 99.24) and  $99.2 \pm 1.0\text{ cm}^{-1}$ , respectively. The depth of Aziz's [10] empirical potential, equal to  $99.55\text{ cm}^{-1}$ , is farther from the experimental value than our result (although well within experimental error bars).

The very good agreement of our potential with the experimental depth of the true argon–argon potential is to some extent due to cancellations of contributions between higher levels of theory neglected by us. We know from the work of Slavicek *et al.* [54] that the complete triples correction, i.e. the difference between the complete coupled clusters approach up to triple excitations (CCSDT) and CCSD(T), is positive ( $0.6\text{ cm}^{-1}$  contribution to the interaction energy at the minimum) and, therefore, diminishes the agreement with experiment. This contribution may be offset by effects of quadruple and higher excitations which are presently unknown. It may also be offset by the relativistic effects which have been computed by Faas *et al.* [86] to contribute  $-0.7\text{ cm}^{-1}$  to the interaction energy at the minimum.

Although the present work was initially aimed at developing an accurate potential at the very strongly repulsive region, evaluations of the quality of our results

in the whole range of interatomic separations suggest that the present potential may actually be the overall most accurate representation of the argon–argon interaction. It is clearly the best representation for energies larger than  $\sim 1\text{ eV}$ , all the way up to nearly 10 keV, i.e. to the upper limit probed by experiments. This statement is based on the excellent agreement for very high energies with the potential of Phelps *et al.* [13] developed to represent this region and on the agreement in the range 1–10 eV with the pointwise potential obtained by a direct inversion of experimental data by Rol [72]. For very large  $R$ , our potential becomes nearly exact due to the use of the very accurate asymptotic constant [67]. In the minimum region, it is difficult to tell whether our potential or the empirical Aziz [10] potential is more accurate. Two characteristic parameters, the depth of the potential and the dissociation energy, are closer to the experimental values for our potential than for Aziz's. On the other hand, the vibrational quanta are better reproduced by the latter potential. The Aziz potential's ground-state rotational constant is closer to experiment if the comparison is made to the original value of Herman *et al.* [70], but the one predicted by our potential is closer to the value recommended by Boyes [12]. Compared to the potentials of Aziz and Slaman [14] and Aziz [10], our potential was tested on a much smaller number of observables. Additional tests, to be performed in the near future, will provide an ultimate evaluation of its quality. Also, the work on a further refinement of our potential by including effects of higher excitations and possibly the relativistic effects is in progress in our group. Another refinement will come from using core-valence optimized basis sets to describe the core contributions to the interaction energy and from CBS extrapolations of these quantities.

The virial coefficients computed with our potential have been critically compared to experimental data. The accuracy of the theoretical potential allowed us to evaluate the quality of various measurements. Based on these evaluations, we suggest that the set of reference virial coefficients from the compilation by Dymond and Smith [78], recommended by the CRC Handbook [85], should be replaced by a combination of theoretical data and the most recent measurements by Tegeler *et al.* [83].

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