



Ab initio pair potential energy curve for the argon atom pair and thermophysical properties of the dilute argon gas. I. Argon-argon interatomic potential and rovibrational spectra

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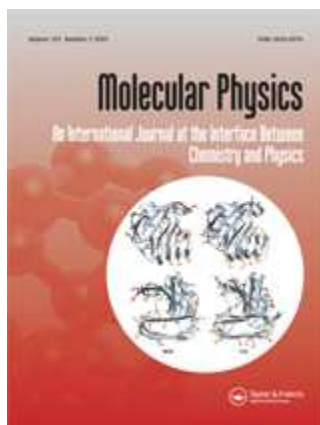
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Ab initio pair potential energy curve for the argon atom pair and thermophysical properties of the dilute argon gas.

I. Argon-argon interatomic potential and rovibrational spectra

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An argon-argon interatomic potential energy curve was derived from quantum-mechanical *ab initio* calculations using basis sets of up to d-aug-cc-pV(6+d)Z quality supplemented with bond functions and *ab initio* methods up to CCSDT(Q). In addition, corrections for relativistic effects were determined. An analytical potential function was fitted to the *ab initio* values and utilized to compute the rovibrational spectrum. The quality of the interatomic potential function was tested by comparison of the calculated spectrum with experimental ones and those derived from other potentials of the literature. In a following paper the new interatomic potential is used to determine selected thermophysical properties of argon by means of quantum-statistical mechanics and the corresponding kinetic theory considering two-body and three-body interactions.

Keywords: argon *ab initio* pair potential; argon analytical potential function; rovibrational spectra.

1 Introduction

The properties of rare gases are of considerable interest for both the development of modeling techniques and as standard values for experiments. Moreover, argon is of special interest in the field of metrology. For the determination of thermophysical fluid properties the knowledge of the potential energy curve between two rare gas atoms is required. Recently, we demonstrated that for helium and neon highly accurate pair potentials can be calculated *ab initio*, i.e. purely from theory [1,2]. The resulting thermophysical properties [3,4] were found to be more accurate than experimental values and can therefore be utilized for calibration of high precision measuring instruments. Since argon is one of the pioneer substances of molecular modeling and a low price alternative for calibration issues, a pair potential of high quality is needed.

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1 Aziz and coworkers [5–7] as well as Boyes [8] followed the standard approach and
2 fitted analytical potential functions to experimental data such as transport proper-
3 ties, pressure virial coefficients, acoustic virial coefficients and rovibronic spectra.
4 These empirical potentials allow the description of low density argon with high ac-
5 curacy for certain temperature ranges. However, for extreme temperature regions
6 their reliability is questionable because of the lack of high precision experimental
7 values.

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11 The computational feasibility of highly correlated *ab initio* methods such as
12 the Møller-Plesset perturbation theory (MP2,MP3,MP4) and the coupled-cluster
13 approach (CC) opened the door to calculations of potential curves entirely from
14 theory. Utilizing MP4 Chalaśiński *et al.* [9] calculated the potential energy between
15 two argon atoms underestimating the well depth compared to the Boyes potential
16 [8] by about 25%. A reduced error of 13% resulted from computations with the
17 interacting correlated fragments approach (ICF) carried out by McLean *et al.* [10].
18 By the introduction of the coupled-cluster approach with full iterative single and
19 double excitations and non-iterative perturbational treatment of triple excitations
20 (CCSD(T) [11]) in combination with the new augmented correlation-consistent
21 basis sets (aug-cc-pVXZ) by Woon and Dunning [12] a considerable improvement
22 in accuracy was achieved. The well depth of the potential calculated by Woon [13] at
23 the frozen-core CCSD(T) level using basis sets up to d-aug-cc-pVQZ and complete
24 basis set (CBS) extrapolation deviated only by 6% from the empirical value. Van
25 Mourik *et al.* [14] decreased the error by another 3% utilizing basis sets up to d-aug-
26 cc-pV6Z, CBS extrapolation and corrections for the effects of core-core and core-
27 valence correlation. Additional midbond functions (3s3p2d1f1g) and the d-aug-cc-
28 pV5Z basis set were used by Fernandez and Koch [15] to enhance the convergence
29 of the correlation energy, so that the well depth of their potential was only about
30 2% too small. Comparable results were obtained by Cybulski and Toczyłowski [16]
31 with the aug-cc-pV5Z basis set and midbond functions (3s3p2d2f1g).

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33 A similar approach was used by Slavíček *et al.* [17], who calculated the interac-
34 tion energies with the aug-cc-pV6Z basis set and midbond functions (3s3p2d2f1g)
35 at the frozen-core CCSD(T) level of theory. They also accounted for the effects
36 of core-core and core-valence correlation, that increased the well depth consider-
37 ably. However, they overestimated this correction by using an aug-cc-pV5Z basis
38 set with midbond functions instead of more suitable aug-cc-pCVXZ or aug-cc-
39 pwCVXZ basis sets by Peterson and Dunning [18]. Slavíček *et al.* were the first
40 to study the impact of higher CC terms on the Ar-Ar interaction energy, espe-
41 cially the difference between the CCSDT [19] (with full iterative triple excitations)
42 and CCSD(T) levels. Since this term was positive (0.9 K at $R = 0.38$ nm), i.e.
43 decreasing the well depth of the potential, it was neglected in the final potential
44 energy curve. The obtained pair potential was characterized by a well depth ε/k_B
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of 142.331 K at $R_\epsilon = 0.3771$ nm, which was quite close to the empirical values by Boyes ($\epsilon/k_B = 143.223$ K at $R_\epsilon = 0.3764$ nm [8]). Recently, Patkowski *et al.* [20] improved the results by extrapolating the SCF interaction energy and the correlation part of the interaction energy calculated by Slavíček *et al.* [17] separately to the CBS limit. Adding the core corrections from [17] they obtained a well depth of 142.83 K at $R_\epsilon = 0.3767$ nm.

Due to the fact, that the last two potentials are questionable with regard to the values of the core correction and the neglect of higher CC-terms and relativistic effects, we developed a new *ab initio* potential energy curve for the argon atom pair. This potential takes into account very high levels of CC-theory as well as accurate corrections for core correlation and relativistic effects. The characteristic properties of the ^{40}Ar - ^{40}Ar rovibrational spectrum were calculated for our potential energy curve and other potentials from the literature in order to validate the results against experimental spectra.

2 Computation of the Ar-Ar pair potential

Following the general pathway described for neon in [2] we performed quantum chemical calculations on the argon atom pair for 38 different Ar-Ar distances between $R = 0.18$ nm and $R = 1.50$ nm. The interaction energies were determined by the supermolecular approach including a full counterpoise correction [21] given by:

$$V(R) = \Delta E_{\text{Ar-Ar}}(R) = E_{\text{Ar-Ar}}(R) - 2 E_{\text{Ar-Q}}(R), \quad (1)$$

where $E_{\text{Ar-Q}}(R)$ is the energy of an argon monomer with a complete dimer basis, i.e. with a ghost basis set at the distance R .

Starting at the CCSD(T) level of theory in the frozen-core approximation we computed the energies utilizing the d-aug-cc-pV(5+d)Z and d-aug-cc-pV(6+d)Z basis sets augmented by a set of midbond functions (4s4p3d3f2g) located at the center between the two atoms. The exponents of the bond functions are: *sp*: 0.06, 0.18, 0.54, 1.62; *df*: 0.15, 0.45, 1.35; *g*: 0.3, 0.9. Dunning *et al.* proposed the cc-pV(X+d)Z series of basis sets [22] for elements of the third row by introducing an additional set of d-functions to the cc-pVXZ basis sets in order to improve the convergence of the atomic SCF-energies towards the CBS limit. We observed, that this improved behavior holds also for the SCF-part of the interaction energies. This is illustrated in Figure 1, which shows interaction energies calculated for the d-aug-cc-pV(X+d)Z + (4s4p3d3f2g) (as from now abbreviated as daVXdZ+(44332)) and the d-aug-cc-pVXZ (daVXZ+(44332)) basis sets for $X = 3 - 6$ at $R = 0.38$ nm.

The CBS-extrapolated values of the correlation part of the interaction energy were obtained by using the results from the CCSD(T) calculations with the daVXdZ+(44332) basis sets ($X = 5, 6$) applying the basis set extrapolation for-

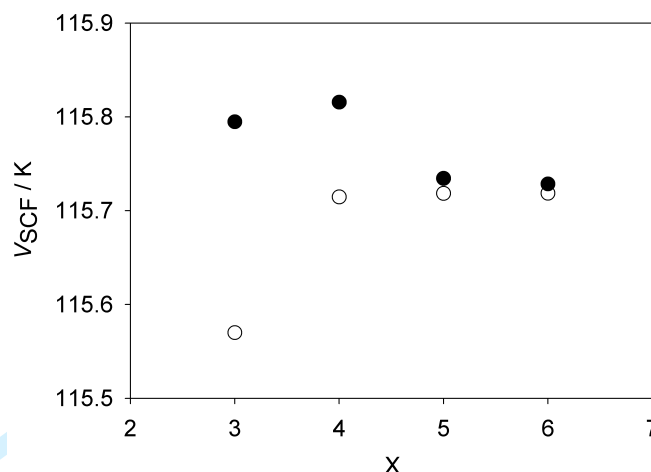


Figure 1. Dependence of the SCF-part of the interaction energy on the basis set type and size at $R = 0.38$ nm. $\circ$ — represent the results for the daVXdZ+(44332) basis set, $\bullet$ — correspond to the daVXZ+(44332) values.

mula proposed by Halkier *et al.* [23]:

$$V_{\text{CCSD(T) corr}}^{\text{daVXdZ}} = V_{\text{CCSD(T) corr}}^{\text{CBS}} + \alpha X^{-3}. \quad (2)$$

With the daV6dZ+(44332) basis set the SCF interaction energies were found to be converged so that these results were not extrapolated. It is highly satisfactory that our final estimate for the CCSD(T) energy of -140.184 K at $R = 0.38$ nm is almost identical to the value obtained by Patkowski *et al.* [20] (-140.182 K at $R = 0.38$ nm), although the basis sets are different.

Crucial improvement of the potential energy curve was achieved by adding several corrections to the interaction energy, namely corrections for the impact of missing core-core and core-valence correlation, for relativistic effects and for the neglect of higher CC terms:

$$V = V_{\text{CCSD(T)}}^{\text{CBS}} + \Delta V_{\text{core}} + \Delta V_{\text{rel}} + \Delta V_{\text{T-(T)}} + \Delta V_{\text{(Q)}}. \quad (3)$$

Calculating the differences between the interaction energies with and without frozen-core approximation the influence of core-core and core-valence electron correlation was accounted for. Van Mourik *et al.* [14] used the dawCVXZ series of basis sets ($X = \text{D, T, Q}$) [18] and obtained the following results for the core corrections: -0.85 K at $R = 0.405$ nm for DZ, -1.07 K at $R = 0.386$ nm for TZ and -1.13 K at $R = 0.381$ nm for QZ. Furthermore, they extrapolated the correction to the CBS limit ($\Delta V_{\text{core}} = -1.14$ K at the minimum of the potential). However, Slavíček *et al.* and Patkowski *et al.* respectively utilized core corrections computed with an aV5Z+(33221) basis set, what is certainly not appropriate due to the construction of this basis set for frozen-core calculations. Their value of -2.2 K at $R = 0.38$ nm

overestimates the effect substantially. Hence, we used the awCV5Z basis set [18] and obtained a value for the core correction of -1.07 K at $R = 0.38$ nm. Considering the different interatomic separations and basis sets this result is quite close to the data of Van Mourik *et al.* Generally, ΔV_{core} was found to be increasingly important in the repulsive region (-650 K at $R = 0.18$ nm).

At the same all-electron CCSD(T)/awCV5Z level the scalar relativistic effects were calculated by means of the Cowan-Griffin approximation [24]. The resulting correction to the interaction energy ΔV_{rel} is negativ for all distances and regarding its size comparable to the core correction. Faas *et al.* [25] estimated the relativistic effect on the well depth to be about -1.0 K using their so-called scaled-ZORA MP2 approach. Taking into account the different Ar-Ar separations and the unequal level of theory, i.e. MP2 instead of CCSD(T), this value is very close to our results (-1.05 K at $R = 0.37$ nm and -0.75 K at $R = 0.38$ nm).

The differences in the interaction energies between the CCSDT method and the more approximative CCSD(T) approach were computed at the frozen-core level utilizing a daVQZ+(3321) basis set with the following exponents of the bond functions: *sp*: 0.1, 0.3, 0.9; *d*: 0.25, 0.75; *f*: 0.45. Contrary to the results for neon [2] $\Delta V_{\text{T-(T)}}$ is positive at all distances. Our values are considerably larger than the ones by Slavíček *et al.* [17] calculated with an aVTZ+(332) basis set (e.g. 1.49 K vs. 0.86 K at $R = 0.38$ nm).

Moreover, the impact of a perturbational treatment of quadruple excitations on the interaction energy $\Delta V_{\text{(Q)}}$ was investigated using the CCSDT(Q) method [26,27] by calculating the differences between the CCSDT(Q) and the CCSDT levels with the aVTZ+(3321) basis set. We surprisingly found this effect to be -2.0 K near the equilibrium distance ($R = 0.38$ nm), what is about one order of magnitude larger than for neon [2]. Hence, this effect is essentially needed to bring the *ab initio* pair potentials for argon into agreement with the empirical ones. Because of numerical inaccuracies for some larger values of R the results for distances between $R = 0.54$ nm and $R = 0.70$ nm had to be smoothed with a polynomial fitted to the ratio of $\Delta V_{\text{(Q)}}$ and $V_{\text{CCSD(T) corr}}^{\text{daV6dZ}}$. For $R = 0.38$ nm we were also able to test the error in using the perturbational instead of the full iterative treatment of the quadruple excitations (CCSDTQ [28]) in analogy to $\Delta V_{\text{T-(T)}}$. This difference was, at least with an aVDZ+(3321) basis set, only 0.10 K. Taking into consideration the enormous computational effort for the CCSDTQ method this effect was neglected.

All CCSD(T) and CCSDT calculations were performed with the Mainz-Austin-Budapest version of ACES II [29]. Utilizing the general CC code MRCC of Kállay [30] the computations at the CCSDT(Q) and CCSDTQ level of theory were realized. The results of all *ab initio* calculations are given in Tables 1 and 2.

Eventually, the parameters of a modified Tang-Toennies potential function [31]

were fitted to the *ab initio* interaction energies:

$$V(R) = A \exp(a_1 R + a_2 R^2 + a_{-1} R^{-1} + a_{-2} R^{-2}) - \sum_{n=3}^8 \frac{C_{2n}}{R^{2n}} \left[1 - \exp(-bR) \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \right]. \quad (4)$$

The dispersion coefficients C_6 , C_8 and C_{10} as well as the coefficients A , a_1 , a_2 , a_{-1} , a_{-2} and b were fitted independently. The higher dispersion coefficients were simultaneously determined within the fit using the recursion formula [31]:

$$C_{2n} = C_{2n-6} \left(\frac{C_{2n-2}}{C_{2n-4}} \right)^3, \quad n \geq 6. \quad (5)$$

Calculated and fitted potential energies differ by less than $\pm 0.1\%$ for distances smaller than 0.90 nm and by up to $\pm 0.3\%$ for $R \geq 0.90$ nm respectively. The resulting potential function is characterized by a well depth of 143.123 K at a distance of $R = 0.3762$ nm, which comes very close to the corresponding values by Boyes [8] ($\varepsilon/k_B = 143.223$ K at $R_\varepsilon = 0.3764$ nm). The fitted dispersion coefficients are in very good agreement with those derived from dipole oscillator strength distributions (C_6) by Kumar and Meath [32] and from many-body perturbation theory (C_8 and C_{10}) by Thakkar *et al.* [33]. All potential parameters are shown in Table 3.

3 Rovibronic spectra of the argon dimer

Since the comparison of calculated and experimental rovibronic spectra is a very stringent test of any pair potential we calculated the energy differences for the rovibrational transitions of the electronic ground state of the $^{40}\text{Ar}-^{40}\text{Ar}$ dimer with the program LEVEL 7.7 by Le Roy [34]. Beside our results Tables 4 and 5 include the values derived from measurements by Coulborn and Douglas [35] and Herman *et al.* [36] as well as those calculated from several empirical and *ab initio* potential functions [7, 8, 15, 17, 20]. Generally, seven bound vibrational levels were found for all pair potentials. Douglas and Colborn as well as Herman *et al.* observed six bound levels, whereas the latter group suggested that there may be altogether seven or eight.

The characteristic parameters of the spectra shown in Table 4 demonstrate that the potential of this work is of significantly increased quality compared with the latest *ab initio* potentials in the literature. The potential well depth is less than 0.1% smaller than the values from the empirical reference potentials [7, 8]. One has to consider that the results of Slavíček *et al.* [17] and Patkowski *et al.* [20] would have been even worse if they had included the appropriate core correction and the estimates of $\Delta V_{T-(T)}$ by Slavíček *et al.* The values for the older potential by Cybulski and Toczyłowski [16] deviate much more from the experimental

data. Concerning the dissociation energies D_0 the new potential shows roughly the same improvement as for the well depth. The experimental values for D_e and D_0 from Herman *et al.* [36] differ noticeably from the ones determined by Coulborn and Douglas [35]. Presumably, the way of evaluation of the measured data is the main reason for the deviations. Hence, Boyes [8] reanalyzed the results by Herman *et al.* and obtained somewhat different values, especially for the rotational constants B_ν . Compared with these results our rotational constant for the vibrational ground-state lies within the error bars, whereas the values from the other *ab initio* potentials lie outside. The disagreement between the results calculated with the potentials by Aziz [7] and Boyes [8] is mainly due to this reassessment of the rovibronic data.

The intervals between the purely vibrational energy levels ($J = 0$) represent another quantity for the validation of pair potentials. As shown in Table 5 the agreement with both the most reliable experimental values by Herman *et al.* [36] and the reevaluated data by Boyes [8] is differing with respect to different vibrational quantum numbers. For $\nu = 3$ and $\nu = 4$ our results lie within the given error bars, whereas for $\nu = 0$ the value is just outside. The discrepancy for the vibrational spacings with $\nu = 1$ and $\nu = 2$ was found to be significantly larger, however, it could be decreased compared to former *ab initio* potentials. Taking into account the differences between the results of the two spectroscopic measurements it could be assumed that the true values for some of the vibrational intervals lie slightly outside the error bars given by Herman *et al.*

4 Summary and conclusions

Utilizing basis sets of up to d-aug-cc-pV(6+d)Z quality with bond functions the interaction energies for the argon atom pair were computed for various interatomic separations at the CCSD(T) level. Furthermore, corrections for core-core and core-valence correlation, for scalar relativistic effects and for higher-order coupled-cluster excitations up to CCSDT(Q) were calculated. It was found that all these effects are of comparable magnitude. Hence, all of them have to be included for highly accurate *ab initio* potential energy curves of the argon atom pair.

The parameters of an analytical potential function were fitted to the *ab initio* values. Eventually, the characteristic rovibrational properties of the $^{40}\text{Ar}-^{40}\text{Ar}$ dimer in the electronic ground state were determined. These results were compared both with values calculated for other potential energy curves from the literature and with highly accurate experimental data. It was found that the new potential is in close agreement with the empirical potentials by Aziz and Boyes [7, 8] and shows considerable improvement compared to older *ab initio* potentials. Since comparison with rovibrational data mainly represents a test of the potential well, we intent to

show computational results for transport properties of the dilute argon gas, which are essentially dependent on the repulsive part of the potential, in the second paper of this series [37]. Furthermore, this paper will include comparison of calculated and experimentally determined second and third pressure virial coefficients as well as second acoustic and dielectric virial coefficients.

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Table 1. Ar-Ar SCF and CCSD(T) interaction energies for the daV5dZ+(44332) and daV6dZ+(44332) basis sets and the extrapolated CCSD(T) values. All energies are in Kelvin.

<i>R</i> /nm	V(SCF)		V(CCSD(T))		extrapolated
	daV5dZ+(44332)	daV6dZ+(44332)	daV5dZ+(44332)	daV6dZ+(44332)	
0.18	112186.342	112141.930	100595.611	100404.502	100202.993
0.20	60087.052	60070.816	52406.333	52299.655	52175.420
0.22	31443.934	31437.972	26313.728	26253.267	26178.407
0.24	16177.214	16175.002	12725.839	12691.769	12648.008
0.26	8211.837	8211.055	5875.323	5856.414	5831.515
0.28	4121.835	4121.546	2531.132	2520.846	2507.116
0.30	2048.765	2048.645	959.954	954.535	947.256
0.31	1439.643	1439.570	536.960	533.091	527.876
0.32	1009.558	1009.517	260.069	257.347	253.663
0.33	706.597	706.578	83.299	81.414	78.851
0.34	493.657	493.649	-25.614	-26.893	-28.639
0.35	344.301	344.298	-89.143	-89.988	-91.146
0.36	239.746	239.746	-122.823	-123.361	-124.099
0.37	166.689	166.689	-137.295	-137.617	-138.060
0.38	115.728	115.729	-139.772	-139.945	-140.184
0.39	80.239	80.239	-135.080	-135.156	-135.259
0.40	55.562	55.562	-126.407	-126.419	-126.437
0.41	38.428	38.428	-115.810	-115.785	-115.751
0.42	26.547	26.547	-104.589	-104.541	-104.475
0.43	18.319	18.320	-93.531	-93.468	-93.381
0.44	12.628	12.629	-83.083	-83.009	-82.909
0.45	8.696	8.697	-73.474	-73.394	-73.285
0.46	5.983	5.984	-64.794	-64.711	-64.599
0.48	2.824	2.826	-50.196	-50.122	-50.022
0.50	1.328	1.330	-38.894	-38.837	-38.762
0.52	0.622	0.624	-30.264	-30.224	-30.172
0.54	0.290	0.292	-23.705	-23.676	-23.639
0.56	0.134	0.136	-18.710	-18.689	-18.662
0.59	0.042	0.043	-13.321	-13.308	-13.293
0.62	0.013	0.014	-9.656	-9.649	-9.642
0.65	0.004	0.004	-7.119	-7.117	-7.114
0.70	0.000	0.001	-4.432	-4.432	-4.434
0.75	0.000	0.000	-2.863	-2.864	-2.867
0.80	0.000	0.000	-1.908	-1.910	-1.912
0.90	0.000	0.000	-0.917	-0.918	-0.919
1.00	0.000	0.000	-0.478	-0.479	-0.479
1.20	0.000	0.000	-0.157	-0.157	-0.157
1.50	0.000	0.000	-0.040	-0.040	-0.040

Table 2. Corrections to the extrapolated CCSD(T) interaction energies and the final potential values. All energies are in Kelvin.

R/nm	ΔV_{core} awCV5Z	ΔV_{rel} awCV5Z	$\Delta V_{\text{T-(T)}}$ daVQZ+(3321)	$\Delta V_{\text{(Q)}}$ aVTZ+(3321)	$V(R)$
0.18	-650.297	-629.600	104.982	-79.607	98948.472
0.20	-395.120	-390.735	65.413	-48.779	51406.200
0.22	-230.501	-221.294	41.590	-31.866	25736.338
0.24	-130.109	-118.251	26.678	-21.706	12404.620
0.26	-71.418	-60.662	17.198	-15.205	5701.427
0.28	-38.215	-30.183	11.131	-10.826	2439.023
0.30	-19.942	-14.673	7.248	-7.754	912.136
0.31	-14.266	-10.161	5.869	-6.563	502.756
0.32	-10.135	-7.011	4.766	-5.559	235.724
0.33	-7.146	-4.825	3.884	-4.706	66.058
0.34	-4.997	-3.316	3.177	-3.978	-37.753
0.35	-3.462	-2.278	2.610	-3.367	-97.643
0.36	-2.373	-1.568	2.154	-2.841	-128.726
0.37	-1.605	-1.084	1.787	-2.404	-141.366
0.38	-1.068	-0.754	1.490	-2.030	-142.546
0.39	-0.695	-0.530	1.249	-1.717	-136.953
0.40	-0.439	-0.378	1.053	-1.457	-127.658
0.41	-0.266	-0.274	0.893	-1.232	-116.630
0.42	-0.150	-0.203	0.761	-1.047	-105.114
0.43	-0.074	-0.154	0.652	-0.892	-93.849
0.44	-0.025	-0.120	0.562	-0.760	-83.251
0.45	0.005	-0.096	0.487	-0.648	-73.536
0.46	0.023	-0.078	0.424	-0.556	-64.786
0.48	0.037	-0.056	0.325	-0.412	-50.128
0.50	0.037	-0.042	0.254	-0.311	-38.825
0.52	0.032	-0.033	0.200	-0.233	-30.207
0.54	0.026	-0.027	0.160	-0.180	-23.660
0.56	0.020	-0.022	0.130	-0.140	-18.674
0.59	0.014	-0.017	0.096	-0.098	-13.298
0.62	0.010	-0.013	0.072	-0.070	-9.643
0.65	0.007	-0.010	0.055	-0.051	-7.113
0.70	0.004	-0.007	0.036	-0.031	-4.432
0.75	0.002	-0.004	0.024	-0.020	-2.865
0.80	0.001	-0.003	0.016	-0.013	-1.911
0.90	0.001	-0.002	0.008	-0.006	-0.918
1.00	0.000	-0.001	0.004	-0.003	-0.479
1.20	0.000	0.000	0.001	-0.001	-0.156
1.50	0.000	0.000	0.000	0.000	-0.040

Table 3. Potential parameters

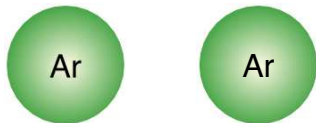
Parameter	Unit	Value	Reference values		
A	K	4.61330146×10^7			
a_1	$(\text{nm})^{-1}$	2.98337630			
a_2	$(\text{nm})^{-2}$	$9.71208881 \times 10^{-2}$			
a_{-1}	nm	$2.75206827 \times 10^{-1}$			
a_{-2}	$(\text{nm})^2$	-1.01489050			
b	$(\text{nm})^{-1}$	4.02517211			
C_6	$\text{K}(\text{nm})^6$	$4.42812017 \times 10^{-1}$	4.45856×10^{-1}	(32)	
C_8	$\text{K}(\text{nm})^8$	$3.26707684 \times 10^{-2}$	3.15180×10^{-2}	(33)	
C_{10}	$\text{K}(\text{nm})^{10}$	$2.45656537 \times 10^{-3}$	2.66773×10^{-3}	(33)	
C_{12}	$\text{K}(\text{nm})^{12}$	$1.88246247 \times 10^{-4}$			
C_{14}	$\text{K}(\text{nm})^{14}$	$1.47012192 \times 10^{-5}$			
C_{16}	$\text{K}(\text{nm})^{16}$	$1.70063432 \times 10^{-6}$			
ε/k_B	K	143.12	142.33 [17]	142.83 [20]	143.22 [8]
R_ϵ	nm	0.3762	0.3771 [17]	0.3767 [20]	0.3764 [8]
σ	nm	0.3357			

Table 4. Equilibrium internuclear distance R_ϵ , dissociation energy D_e , vibrational-ground-state dissociation energy D_0 , and the rotational constant B_0 of the $^{40}\text{Ar}-^{40}\text{Ar}$ dimer in the electronic ground state.

R_ϵ	D_e	D_0	B_0	Reference
nm	cm^{-1}	cm^{-1}	cm^{-1}	
0.3759	99.55	84.75	0.05778	35
0.3761	99.20	84.47	0.05776 ± 0.00006	36
0.3757	99.55	84.75	0.05777	7
0.3764	99.54	84.74	0.05755 ± 0.00011	8
0.3778	96.99	82.38	0.05708	16
0.3771	98.93	84.16	0.05745	17
0.3767	99.27	84.38	0.05743	20
0.3762	99.48	84.64	0.05760	this work

Table 5. Observed and calculated vibrational intervals $\Delta G_{\nu+1/2}$ in cm^{-1} for the electronic ground state of $^{40}\text{Ar}_2$

ν	experiment		empirical potentials		ab initio potentials			
	Ref. 35	Ref. 36	Ref. 7	Ref. 8	Ref. 16	Ref. 17	Ref. 20	this work
0	25.74	25.69±0.01	25.68	25.68±0.02	25.27	25.58	25.75	25.71
1	20.41	20.58±0.02	20.56	20.59±0.02	20.11	20.44	20.48	20.52
2	15.60	15.58±0.02	15.58	15.57±0.02	15.15	15.46	15.44	15.52
3	10.91	10.91±0.03	10.92	10.87±0.02	10.55	10.78	10.79	10.88
4	6.78	6.84±0.07	6.83	6.82±0.07	6.53	6.74	6.76	6.82



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