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# State-of-the-art *ab initio* potential energy curve for the krypton atom pair and thermophysical properties of dilute krypton gas

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A new reference krypton-krypton interatomic potential energy curve was developed by means of quantum-chemical *ab initio* calculations for 36 interatomic separations. Highly accurate values for the interaction energies at the complete basis set limit were obtained using the coupled-cluster method with single, double, and perturbative triple excitations as well as t-aug-cc-pV5Z and t-aug-cc-pV6Z basis sets including mid-bond functions, with the 6Z basis set being newly constructed for this study. Higher orders of coupled-cluster terms were considered in a successive scheme up to full quadruple excitations. Core-core and core-valence correlation effects were included. Furthermore, relativistic effects were studied not only at a scalar relativistic level using second-order direct perturbation theory, but also utilizing full four-component and Gaunt-effect computations. An analytical pair potential function was fitted to the interaction energies, which is characterized by a depth of 200.88 K with an estimated standard uncertainty of 0.51 K. Thermophysical properties of low-density krypton were calculated for temperatures up to 5000 K. Second and third virial coefficients were obtained from statistical thermodynamics. Viscosity and thermal conductivity as well as the self-diffusion coefficient were computed using the kinetic theory of gases. The theoretical results are compared with experimental data and with results for other pair potential functions from the literature, especially with those calculated from the recently developed *ab initio* potential of Waldrop *et al.* [J. Chem. Phys. **142**, 204307 (2015)]. Highly accurate experimental viscosity data indicate that both the present *ab initio* pair potential and the one of Waldrop *et al.* can be regarded as reference potentials, even though the quantum-chemical methods and basis sets differ. However, the uncertainties of the present potential and of the derived properties are estimated to be considerably lower. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943959>]

## I. INTRODUCTION

In the course of theoretical investigations of intermolecular interactions, noble gases have become valuable model substances. This is not only because of the simple spherically symmetric nature of the pair potential, which allows the use of very accurate theoretical methods for the calculation of thermophysical and other properties, but also due to the applicability of high-level quantum-chemical *ab initio* approaches. Studies on helium over two decades led to a state where thermophysical properties calculated from *ab initio* pair potentials are far more reliable than the best experimental data.<sup>1–3</sup> Therefore, theoretical property predictions for helium can be used as calibration standards, e.g., for relative gas viscosity measurements.<sup>4,5</sup> For neon, our group developed a pair potential of reference quality,<sup>6</sup> and later we<sup>7,8</sup> as well as Patkowski and Szalewicz<sup>9</sup> thoroughly investigated the argon dimer potential. The derived thermophysical property data for gaseous neon<sup>10</sup> and argon<sup>11,12</sup> again show reference character, although their estimated uncertainties are considerably larger than those for helium due to the less accurate quantum-chemical approaches feasible for neon and argon.

For a long time, the reference potential for the krypton dimer has been the empirical potential energy curve of Aziz and co-workers<sup>13,14</sup> with a well depth of  $\varepsilon/k_B = 201.3$  K, where  $k_B$  is Boltzmann's constant. It was fitted to accurate low-density viscosity data as well as to vibrational properties of the dimer and beam scattering data. Haley and Cybulski<sup>15</sup> as well as Slavíček *et al.*<sup>16</sup> were the first to develop *ab initio* pair potentials for krypton based on the coupled-cluster method with single, double, and perturbative triple excitations, CCSD(T),<sup>17</sup> which is the standard approach for accurate computations of weak molecular or atomic interactions. Haley and Cybulski used the frozen-core (FC) approximation and correlation consistent basis sets up to aug-cc-pV5Z (abbreviated as aV5Z) supplemented with additional mid-bond functions. At the highest level applied, their pair potential is characterized by a well depth of  $\varepsilon/k_B = 191.01$  K. The potential recommended by Slavíček *et al.* was developed using the aVQZ-PP basis set,<sup>18</sup> which uses an effective core potential, and bond functions. It has a well depth of 196.37 K. As the authors discussed, further corrections for core-core and core-valence correlation, for relativistic effects, and for higher excitations within the coupled-cluster approach are of special importance for the heavier noble gases and have to be considered for quantitative predictions of the potential energy curve.

Recently, Waldrop *et al.*<sup>19</sup> presented a thorough study on the pair potential of krypton and derived transport

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properties of dilute krypton gas. Their quantum-chemical approach included not only a complete basis set (CBS) extrapolation of the correlation energy based on explicitly correlated coupled-cluster calculations, but also all corrections suggested by Slavíček *et al.*,<sup>16</sup> each of them being extrapolated separately to the CBS limit. Coupled-cluster methods beyond CCSD(T) were taken into account using a correction term for the CCSDT(Q) approach<sup>20</sup> with basis sets up to aVQZ quality. Waldrop *et al.* accounted for core-core and core-valence correlation effects by calculating the difference between the FC and the all-electron (AE) CCSD(T) interaction energies using specialized basis sets from the aug-cc-pwCVXZ (awCVXZ) series<sup>21</sup> up to quintuple-zeta quality. Relativistic effects were considered utilizing the second-order Douglas-Kroll-Hess (DKH) hamiltonian<sup>22,23</sup> at the all-electron CCSD(T) level together with uncontracted aVXZ basis sets. Influences of effects beyond the scalar relativistic approximation were reported to be negligible. The final *ab initio* interaction energies were used to obtain the parameters of an analytical potential function of the Hartree-Fock-dispersion (HFD) type including dispersion terms with  $R^{-6}$  and  $R^{-8}$  dependence, where  $R$  is the interatomic distance. Waldrop *et al.* reported a well depth of 201.52 K with an estimated combined standard uncertainty of 1.1 K. This result is very close to the pair potential of Aziz and co-workers,<sup>13,14</sup> supported by the comparison of derived viscosity data for dilute krypton with the most accurate experimental values. However, the perfect agreement for the viscosity at room temperature with the reference value of Berg and Burton<sup>4</sup> is to some extent a fortunate coincidence due to the relatively large accepted fitting errors ranging from 0.18 K for the near-minimum distance of 4 Å to  $-2.26$  K for  $R = 3.2$  Å.

In the present study, we employed an improved quantum-chemical approach for the determination of the interaction energies of the krypton atom pair. Following Patkowski,<sup>24</sup> we believe that standard orbital coupled-cluster calculations can be regarded as slightly more reliable for this purpose compared to explicitly correlated ones. A new aV6Z basis set (see Sec. II A) was developed to improve the CBS convergence of the correlation energy. Discrepancies for the CBS values of the interaction energy between the standard CCSD(T) and explicitly correlated approaches are discussed in Sec. II B. Section II C describes the post-CCSD(T) correlation effects, where a stepwise approach up to the coupled-cluster level with full single, double, triple, and quadruple excitations, CCSDTQ,<sup>25,26</sup> is applied. Sections II D and II E are concerned with corrections to the FC approximation and with relativistic effects, respectively. The latter issue is investigated with a special focus on corrections beyond the scalar relativistic level. Furthermore, in Sec. II G, we discuss the deviations of the nonadditive *ab initio* three-body interaction energy from the Axilrod-Teller-Muto (ATM) model.<sup>27,28</sup> The analytical function for the *ab initio* pair potential and the derived vibrational spectrum are discussed in Sec. III. Second and third virial coefficients of krypton calculated from the theoretical pair potential and two models for the nonadditive three-body interaction are presented in Sec. IV. In Sec. V, the transport properties of dilute krypton

gas computed using different pair potentials are compared with experimental data.

## II. QUANTUM-CHEMICAL CALCULATIONS

All interaction energies presented in this study were calculated using the supermolecular approach including the full counterpoise correction of Boys and Bernardi.<sup>29</sup> Quantum-chemical basis sets were formed from the correlation consistent basis sets developed by Wilson *et al.*<sup>30</sup> (aVXZ with  $X = D, T, Q, 5$ ) and by DeYonker *et al.*<sup>21</sup> (awCVXZ with  $X = D, T, Q, 5$ ) as well as from the aV6Z basis set developed for the present study. Additional diffuse functions leading to doubly and triply augmented basis sets (daVXZ, taVXZ) were generated in an even-tempered manner from the two most diffuse basis functions within the respective aVXZ basis sets.

Additional bond functions located at the center between the two krypton atoms are utilized to improve the convergence behavior towards the CBS limit in most of the calculations. While Waldrop *et al.*<sup>19</sup> chose bond functions that are identical to the hydrogenic basis functions of the same cardinal number  $X$  used for the krypton atoms, we employed only two sets of bond functions, which have proven to be reliable for the determination of interaction energies between noble gas atoms.<sup>1,6,7</sup> The large set of mid-bond functions, denoted by (44332), is characterized by exponents of 0.06, 0.18, 0.54, and 1.62 for  $s$  and  $p$  functions, 0.15, 0.45, and 1.35 for  $d$  and  $f$  functions, as well as 0.3 and 0.9 for  $g$  functions. The exponents of the smaller set, denoted by (3321), are 0.1, 0.3, and 0.9 for  $s$  and  $p$  functions, 0.25 and 0.75 for  $d$  functions, and 0.45 for a single  $f$  function.

Extrapolations of the correlation part of the interaction energy to the CBS limit were conducted by means of the two-point scheme introduced by Halkier *et al.*,<sup>31</sup>

$$V_{\text{corr,CBS}} = \frac{V_{\text{corr},X}X^3 - V_{\text{corr},X-1}(X-1)^3}{X^3 - (X-1)^3}. \quad (1)$$

Most of the coupled-cluster calculations were performed with the CFOUR program,<sup>32</sup> except for the CCSDT(Q) and CCSDTQ computations, which also involved the MRCC package.<sup>33</sup> For the optimization of the aV6Z basis set, the NWCHEM<sup>34</sup> and GAUSSIAN 03<sup>35</sup> packages were utilized. Four-component relativistic calculations were conducted using the DIRAC program.<sup>36</sup>

### A. Sextuple-zeta basis set for krypton

The general strategy for the development of correlation consistent basis sets was introduced by Dunning<sup>37</sup> for first row elements and later adapted to third row elements by Wilson *et al.*<sup>30</sup> We adopted the procedure described by Wilson *et al.* for the aVXZ series of basis sets ( $X \leq 5$ ) with the following modifications:

- The basic family of possible Hartree-Fock primitive sets was extended to sets with up to 30  $s$ , 19  $p$ , and 14  $d$  type functions.

- The exponents for the polarization functions of  $d$ ,  $f$ , and  $g$  type were optimized using the  $(30s19p14d)/[9s8p1d]$  set instead of the smaller  $(24s16p10d)/[8s7p1d]$  set used by Wilson *et al.*
- For the determination of the appropriate number of primitive functions for the  $s$  and  $p$  contractions, the optimized  $(5d4f3g)$  set of polarization functions was applied instead of the  $(3d2f1g)$  set. The optimal set of Hartree-Fock primitive functions was found to be  $(27s19p13d)$ .
- An additional  $d$  primitive function was included and optimized according to the procedure described by Wilson *et al.*, thus resulting in a  $(27s19p14d)$  set contracted to  $[9s8p6d]$ . The previously optimized  $4f$  polarization set was then added and re-optimized, followed by an equivalent step for the  $3g$  set. Finally, a  $2h$  set and a single  $i$  function were successively optimized.
- Due to the lack of equivalent basis sets for bromine and selenium, the exponents of the augmenting diffuse functions for the aV6Z basis set could not be

determined by extrapolation. Therefore, we estimated the values from the trends observed in the available aVXZ sets for krypton ( $X \leq 5$ ) and for argon ( $X \leq 6$ ).

The parameters of the final aV6Z basis set for krypton, characterized by  $(28s20p15d5f4g3h2i)/[10s9p7d5f4g3h2i]$ , are tabulated in the supplementary material.<sup>38</sup>

## B. Complete basis set limit

The main part of the interaction energy can be determined at the CCSD(T) level of theory with all but the valence-shell electrons treated as frozen orbitals, i.e., only the  $4s$  and  $4p$  electrons are considered for the computation of the correlation energy. When using large correlation consistent basis sets, the SCF part of the interaction energy is sufficiently converged, so that only the correlation part needs to be extrapolated to the CBS limit. In Table I, we compare our results for the interaction energies of the krypton atom pair at the near-minimum distance  $R = 4.0 \text{ \AA}$  for a variety of basis sets with results from the study of

TABLE I. Interaction energies of  $\text{Kr}_2$  for  $R = 4.0 \text{ \AA}$  in Kelvin. “Extr.” corresponds to the CBS-extrapolated values being the sum of the SCF interaction energy for the cardinal number  $X$  and the extrapolated correlation energy for  $X$  and  $X - 1$  according to Eq. (1); (T\*\*) denotes the scaling of the triple excitation contributions within the explicitly correlated CCSD(T) approaches used in Ref. 19; “M” refers to the variable bond functions used in Ref. 19.

Method	Basis set family	$X = 2$ (D)	$X = 3$ (T)	$X = 4$ (Q)	$X = 5$	$X = 6$
This work						
CCSD(T)/FC	aVXZ	-25.12	-118.51	-163.26	-178.30	-183.96
Extr.			-161.14	-196.20	-193.89	-191.70
CCSD(T)/FC	daVXZ	-43.95	-146.45	-174.56	-184.16	-187.83
Extr.			-192.48	-195.10	-194.14	-192.88
CCSD(T)/FC	taVXZ	-48.95	-149.96	-175.78	-185.34	-188.71
Extr.			-194.61	-194.82	-195.30	-193.35
CCSD(T)/FC	aVXZ+(3321)	-171.66	-185.52	-186.03	-188.10	-189.16
Extr.			-192.73	-186.36	-190.25	-190.60
CCSD(T)/FC	daVXZ+(3321)	-174.28	-188.47	-187.69	-189.17	-189.98
Extr.			-195.27	-187.09	-190.70	-191.06
CCSD(T)/FC	taVXZ+(3321)	-176.03	-188.53	-187.82	-189.39	-190.16
Extr.			-195.16	-187.25	-191.02	-191.19
CCSD(T)/FC	aVXZ+(44332)			-188.32	-189.41	-190.06
Extr.					-190.55	-190.94
CCSD(T)/FC	daVXZ+(44332)			-188.73	-189.82	-190.38
Extr.					-190.96	-191.14
CCSD(T)/FC	taVXZ+(44332)			-188.82	-189.91	-190.48
Extr.					-191.06	-191.25
Waldrop <i>et al.</i> <sup>19</sup>						
CCSD(T)/FC	aVXZM	-100.12	-176.05	-186.48	-189.38	
Extr.			-207.67	-194.05	-192.40	
CCSD(T)-F12a/FC	aVXZM	-150.74	-187.65	-190.31	-191.21	
Extr.			-204.22	-192.36	-192.15	
CCSD(T**)-F12a/FC	aVXZM	-168.48	-196.85	-194.42	-193.32	
Extr.			-209.12	-192.67	-192.16	
CCSD(T)-F12b/FC	aVXZM	-137.41	-181.32	-186.13	-188.98	
Extr.			-200.13	-189.66	-191.96	
CCSD(T**)-F12b/FC	aVXZM	-155.16	-190.52	-190.24	-191.09	
Extr.			-203.52	-190.05	-191.98	



Waldrop *et al.*<sup>19</sup> Due to possible imbalances between the atomic basis and the bond function sets, calculations with the (44332) set of bond functions were performed only for the larger atomic basis sets ( $X \geq Q$ ). The results show that the new basis sets of sextuple-zeta quality yield interaction energies which give consistent trends within each of the series of basis sets. The extrapolation of the correlation part to the CBS limit was conducted according to Eq. (1) for each combination of successive basis sets ( $X, X - 1$ ). The extrapolated values combined with the SCF interaction energy for the higher cardinal number add up to the tabulated values for the CCSD(T)/FC level of theory, denoted, for example, by  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV6Z+(44332)}}$ . The extrapolated values for the largest basis sets,  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV5Z+(3321)}}$ ,  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV6Z+(3321)}}$ ,  $V_{\text{CCSD(T)/FC,CBS}}^{\text{daV5Z+(44332)}}$ ,  $V_{\text{CCSD(T)/FC,CBS}}^{\text{daV6Z+(44332)}}$ ,  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV5Z+(44332)}}$ , and  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV6Z+(44332)}}$  agree to within 0.3 K. The reference value, corresponding to the highest basis set level, is  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV6Z+(44332)}} = -191.25$  K. However, this value deviates from the one used by Waldrop *et al.* for their pair potential by +0.73 K. These authors tested the explicitly correlated coupled-cluster approximations CCSD(T)-F12a and CCSD(T)-F12b<sup>39</sup> with and without scaled triple excitation contributions (see Table I) and found that their results for the largest basis set of quintuple-zeta quality are consistent to within 0.2 K.

Another publication concerned with CBS limiting values for interaction energies is the study by Patkowski,<sup>24</sup> where the convergence towards the CBS limit at the CCSD(T)/FC level of theory using standard and explicitly correlated approaches was investigated thoroughly for He<sub>2</sub> through Kr<sub>2</sub>. Explicitly correlated calculations for neon and argon with 5Z basis sets including bond functions yielded CBS values with deviations of about 0.3 K and up to 1.8 K, respectively, from the reference data obtained from standard CCSD(T) computations. The use of sextuple-zeta basis sets increases the agreement considerably. For krypton, where only basis sets up to  $X = 5$  were available, Patkowski estimated the reference CBS value based on standard CCSD(T) calculations to be  $-192.83$  K for  $R = 4.06$  Å. This value results from the average of two different CBS extrapolated interaction energies, one obtained from calculations with a large but constant set of bond functions and the other one using bond functions from the hydrogenic basis set with the same label as the atomic krypton basis set. Our CBS value for  $R = 4.06$  Å extrapolated from taV5Z+(44332) and taV6Z+(44332) interaction energies amounts to  $-192.75$  K, which is in almost perfect agreement with the averaged value of Patkowski. Using the explicitly correlated CCSD(T)-F12b method with scaled triples and aVXZ basis sets with corresponding hydrogen bond functions, Patkowski obtained a CBS value of  $-193.35$  K for  $R = 4.06$  Å, whereas the calculations of Waldrop *et al.* yielded  $V = -193.42$  K. Furthermore, Patkowski computed the CBS interaction energy with the same method but with an invariant set of bond functions, yielding a value of  $-192.39$  K. The deviation of about 1 K illustrates that the CBS extrapolated interaction energies of the krypton dimer based on QZ and 5Z basis sets using explicitly correlated CCSD(T) calculations cannot be regarded as fully converged with respect to the CBS limit and

are dependent on the chosen type of bond functions, which is consistent with the results for the other noble gases. Therefore, it can be concluded that our CBS results based on the new sextuple-zeta basis set are more reliable than the values used by Waldrop *et al.*

### C. Coupled-cluster methods beyond CCSD(T)

Except for the helium dimer, it is not feasible to calculate the interaction energy between noble gas atoms at the full CI level of electron correlation. We adopted the stepwise procedure already used for neon<sup>6</sup> and argon<sup>7</sup> and treated the post-CCSD(T) contributions to the interaction energy as the sum

$$V_{\text{post-CCSD(T)}} = V_{\text{T-(T)}} + V_{\text{Q-T}} + V_{\text{Q-(Q)}}. \quad (2)$$

Here,  $V_{\text{T-(T)}}$  refers to the difference in the interaction energies between the CCSDT<sup>40,41</sup> and CCSD(T)<sup>17</sup> levels of theory,  $V_{\text{Q-T}}$  accounts for the influence of added perturbative quadruple excitations,<sup>20</sup> and  $V_{\text{Q-(Q)}}$  is the difference between the CCSDTQ<sup>25,26</sup> and CCSDT(Q) approaches. All calculations with post-CCSD(T) methods were performed using the FC approximation.

Following Patkowski *et al.*,<sup>9</sup>  $V_{\text{T-(T)}}$  and  $V_{\text{Q-T}}$  were extrapolated to the CBS limit according to Eq. (1). The results for the individual contributions obtained for the test geometry with  $R = 4.0$  Å are shown in Table II along with the results of Waldrop *et al.* Although their extrapolated values for  $V_{\text{T-(T),CBS}}^{\text{aVTZ}} = 3.034$  K and for  $V_{\text{T-(T),CBS}}^{\text{aVQZ}} = 3.004$  K seem to be converged, we obtained a somewhat higher reference value of  $V_{\text{T-(T),CBS}}^{\text{daV5Z+(3321)}} = 3.513$  K. Due to computational limitations,

TABLE II. Differences between interaction energies (in Kelvin) for the krypton dimer at the near-minimum distance  $R = 4.0$  Å calculated for successive approximations of the coupled-cluster method. “Extr.” corresponds to the CBS-extrapolated values for  $X$  and  $X - 1$  according to Eq. (1).

Basis set family	$X = 2$	$X = 3$	$X = 4$	$X = 5$
Difference CCSDT-CCSD(T)				
aVXZ <sup>a</sup>	0.223	2.201	2.666	
Extr. <sup>a</sup>		3.034	3.004	
daVXZ+(3321) <sup>b</sup>	-0.240	2.216	2.907	3.202
Extr. <sup>b</sup>		3.250	3.411	3.513
Difference CCSDT(Q)-CCSDT				
aVXZ <sup>a,b</sup>	-1.171	-1.811	-2.511	
Extr. <sup>a,b</sup>		-2.082	-3.020	
aVXZ+(3321) <sup>b</sup>	-1.467	-2.446	-2.766	
Extr. <sup>b</sup>		-2.858	-3.000	
Difference CCSDTQ-CCSDT(Q)				
aVXZ <sup>b</sup>	0.296			
aVXZ+(3321) <sup>b</sup>	0.212			
Difference CCSDTQ(P)-CCSDTQ				
aVXZ <sup>b</sup>	-0.005			

<sup>a</sup>Waldrop *et al.*<sup>19</sup>

<sup>b</sup>This work.

calculations at the CCSDT(Q) level of theory were restricted to quadruple-zeta basis sets. Since the extrapolated results for  $V_{(Q)-T,CBS}^{aVQZ} = -3.02$  K and for  $V_{(Q)-T,CBS}^{aVQZ+(3321)} = -3.00$  K coincide, we used values obtained without bond functions for  $V_{(Q)-T}$  in accordance with Ref. 19. The combined correction of  $V_{(Q)-T,CBS}^{aVQZ} = -0.016$  K reported by Waldrop *et al.* differs by  $-0.509$  K from our value of  $0.493$  K obtained from the stepwise approach.

The difference between the coupled-cluster level with full iterative and with perturbative treatment of quadruple excitations was computed with the aVDZ+(3321) basis set. The result for  $R = 4.0$  Å is  $V_{Q-(Q)}^{aVDZ+(3321)} = 0.212$  K. It can be concluded from the result for the same basis set without bond functions,  $V_{Q-(Q)}^{aVDZ} = 0.296$  K, that this correction term is satisfactorily converged with respect to the CBS limit. With all three terms, the post-CCSD(T) correction to the interaction energy for  $R = 4.0$  Å amounts to  $V_{\text{post-CCSD(T)}} = 0.705$  K and differs by  $+0.721$  K from the value obtained by Waldrop *et al.* In addition, the interaction energy contribution due to

effects beyond the CCSDTQ level of theory was tested for  $R = 4.0$  Å by means of the CCSDTQ(P)<sup>42</sup> method with the aVDZ basis set yielding  $V_{(P)-Q}^{aVDZ} = -0.005$  K. Although this value can only be regarded as a rough estimate, and the behavior might be somewhat different for other interatomic distances, it can be regarded as evidence that the coupled-cluster series truncated at the CCSDTQ level is sufficient to obtain an accurate full CI estimate for the interaction energy between two krypton atoms. Values for the corrections according to Eq. (2) are shown for all interatomic distances in Table III along with the values for  $V_{\text{CCSD(T)/FC,CBS}}^{\text{taV6Z}+(44332)}$ .

#### D. Core-core and core-valence correlation

Appropriate basis sets for CCSD(T) calculations that include core-core and core-valence correlation effects are the correlation consistent weighted core-valence basis sets (cc-pwCVXZ, abbreviated as wCVXZ) developed by DeYonker *et al.*<sup>21</sup> supplemented with the diffuse functions taken from

TABLE III. Nonrelativistic interaction energies for Kr<sub>2</sub> at the SCF and CCSD(T)/FC levels of theory as well as post-CCSD(T) corrections in Kelvin as a function of the interatomic distance.

$R / \text{Å}$	$V_{\text{SCF}}$	$V_{\text{corr,CBS}}^{\text{taV6Z}+(44332)}$	$V_{\text{CCSD(T)/FC,CBS}}^{\text{taV6Z}+(44332)}$	$V_{T-(T),CBS}^{\text{daV5Z}+(3321)}$	$V_{(Q)-T,CBS}^{aVQZ}$	$V_{Q-(Q)}^{aVDZ+(3321)}$	$V_{\text{post-CCSD(T)}}$
2.2	64 742.674	-8512.320	56 230.354	82.999	-56.779	3.034	29.254
2.4	35 829.010	-6064.710	29 764.300	57.828	-38.329	2.002	21.501
2.6	19 558.578	-4312.761	15 245.816	40.380	-26.831	1.364	14.913
2.8	10 547.758	-3064.161	7 483.597	28.178	-19.298	0.950	9.830
3.0	5 626.389	-2176.482	3 449.906	19.690	-14.122	0.683	6.251
3.2	2 971.551	-1546.510	1 425.042	13.790	-10.417	0.512	3.885
3.3	2 152.109	-1304.100	848.009	11.556	-8.951	0.451	3.056
3.4	1 555.284	-1100.146	455.137	9.704	-7.687	0.400	2.417
3.5	1 121.666	-928.636	193.029	8.154	-6.595	0.358	1.917
3.6	807.363	-784.463	22.900	6.861	-5.650	0.322	1.533
3.7	580.051	-663.307	-83.256	5.784	-4.836	0.290	1.238
3.8	416.002	-561.517	-145.515	4.887	-4.135	0.262	1.013
3.9	297.849	-476.007	-178.158	4.138	-3.534	0.236	0.839
4.0	212.913	-404.165	-191.252	3.513	-3.020	0.212	0.705
4.1	151.967	-343.788	-191.822	2.991	-2.583	0.191	0.599
4.2	108.310	-293.018	-184.707	2.554	-2.210	0.172	0.515
4.3	77.090	-250.292	-173.202	2.188	-1.895	0.154	0.448
4.4	54.797	-214.299	-159.502	1.881	-1.627	0.138	0.393
4.5	38.903	-183.940	-145.037	1.623	-1.400	0.124	0.347
4.6	27.587	-158.294	-130.707	1.405	-1.207	0.113	0.311
4.7	19.540	-136.593	-117.053	1.220	-1.043	0.101	0.278
4.8	13.826	-118.196	-104.370	1.064	-0.904	0.091	0.251
5.0	6.901	-89.258	-82.357	0.818	-0.684	0.073	0.207
5.2	3.432	-68.181	-64.750	0.637	-0.524	0.058	0.172
5.4	1.701	-52.673	-50.973	0.503	-0.405	0.047	0.145
5.6	0.840	-41.137	-40.297	0.401	-0.317	0.038	0.123
5.9	0.290	-28.939	-28.649	0.291	-0.223	0.028	0.096
6.2	0.100	-20.791	-20.691	0.216	-0.161	0.021	0.076
6.5	0.034	-15.225	-15.191	0.162	-0.118	0.016	0.060
7.0	0.006	-9.398	-9.393	0.104	-0.073	0.010	0.041
7.5	0.001	-6.031	-6.030	0.069	-0.047	0.006	0.028
8.0	0.000	-3.999	-3.999	0.047	-0.031	0.004	0.020
9.0	0.000	-1.906	-1.906	0.023	-0.015	0.002	0.010
10.0	0.000	-0.990	-0.990	0.012	-0.008	0.001	0.006
12.0	0.000	-0.322	-0.322	0.004	-0.003	0.000	0.002
15.0	0.000	-0.082	-0.082	0.001	-0.001	0.000	0.001

the corresponding  $aVXZ$  basis sets and with bond functions. These basis sets were not constructed with all electrons correlated within the optimization procedure, but with the inner core ( $1s$ ,  $2s$ , and  $2p$  electrons) treated as frozen orbitals. Therefore, we chose a two-step *ansatz* to account for the effects of core-core and core-valence correlation on the interaction energy. The main part was determined as the difference between the correlation energy obtained from calculations with the inner core treated as frozen (denoted as IFC) and the corresponding value from the standard FC approximation. The results for the near-minimum distance of  $R = 4.0 \text{ \AA}$  are  $V_{\text{IFC-FC}}^{\text{dawCVTZ}+(3321)} = -6.583 \text{ K}$ ,  $V_{\text{IFC-FC}}^{\text{dawCVQZ}+(3321)} = -5.976 \text{ K}$ , and  $V_{\text{IFC-FC}}^{\text{dawCV5Z}+(3321)} = -5.838 \text{ K}$ , leading to CBS-extrapolated values of  $V_{\text{IFC-FC,CBS}}^{\text{dawCVQZ}+(3321)} = -5.720 \text{ K}$  and  $V_{\text{IFC-FC,CBS}}^{\text{dawCV5Z}+(3321)} = -5.692 \text{ K}$  according to Eq. (1). The second step was to determine the difference between the AE and the IFC level of electron correlation, where fully uncontracted  $aVXZ+(3321)$  basis sets were used. Due to the small values of this correction and the good CBS convergence behavior,

extrapolation to the CBS limit was not conducted. For the reference geometry, values of  $V_{\text{AE-IFC}}^{\text{unc-aVTZ}+(3321)} = 0.154 \text{ K}$  and  $V_{\text{AE-IFC}}^{\text{unc-aVQZ}+(3321)} = 0.163 \text{ K}$  were obtained. The total value of the core-correlation correction to the interaction energy for  $R = 4.0 \text{ \AA}$  amounts to

$$V_{\text{AE-FC}} = V_{\text{IFC-FC}}^{\text{dawCV5Z}+(3321)} + V_{\text{AE-IFC}}^{\text{unc-aVQZ}+(3321)} = -5.529 \text{ K}.$$

This is in very good agreement with the value of  $V_{\text{AE-FC,CBS}}^{\text{awCV5Z}} = -5.571 \text{ K}$  obtained by Waldrop *et al.* within their one-step approach using smaller basis sets. In Table IV, the values for  $V_{\text{IFC-FC}}^{\text{dawCV5Z}+(3321)}$  and  $V_{\text{AE-IFC}}^{\text{unc-aVQZ}+(3321)}$  are given for all interatomic distances.

## E. Relativistic effects

A variety of quantum-chemical approaches has been developed for the investigation of relativistic effects on atomic and molecular properties (see, for example, Ref. 43 and references therein). For closed-shell systems consisting of

TABLE IV. Corrections to the interaction energy due to core-core and core-valence correlation and relativistic effects as well as the total interaction energy (Eq. (7)), its estimated combined standard uncertainty, and the fitted pair potential as a function of the interatomic distance. Here, “bf” refers to the (3321) set of bond functions. All energies are in Kelvin.

$R / \text{\AA}$	$V_{\text{IFC-FC,CBS}}^{\text{dawCV5Z}+\text{bf}}$	$V_{\text{AE-IFC}}^{\text{unc-aVQZ}+\text{bf}}$	$V_{\text{DPT2/FC,CBS}}^{\text{dawCV5Z}+\text{bf}}$	$V_{\text{DPT2,IFC-FC}}^{\text{dawCVQZ}+\text{bf}}$	$V_{4\text{eDC-DPT2}}^{\text{unc-aVTZ}+\text{bf}}$	$V_{\text{Gaunt}}^{\text{unc-aVTZ}+\text{bf}}$	$V^{\text{tot}}$	$u_c(V^{\text{tot}})$	$V^{\text{tot}}$ (fitted)
2.2	-1248.330	-2.292	-1910.718	-8.807	-41.980	99.974	53 147.455	68.384	53 149.849
2.4	-784.189	-2.521	-1172.789	0.183	-17.016	62.855	27 872.324	42.574	27 869.802
2.6	-474.763	-1.870	-682.441	2.921	-6.045	37.607	14 136.140	26.266	14 135.936
2.8	-278.380	-1.129	-380.509	3.047	-1.785	21.444	6 856.114	15.921	6 856.382
3.0	-158.479	-0.553	-204.392	2.359	-0.410	11.606	3 106.289	9.473	3 106.365
3.2	-87.656	-0.184	-105.858	1.594	-0.135	5.883	1 242.570	5.533	1 242.577
3.3	-64.473	-0.063	-75.077	1.266	-0.150	4.049	716.617	4.192	716.619
3.4	-47.054	0.025	-52.671	0.987	-0.198	2.700	361.343	3.157	361.336
3.5	-34.054	0.087	-36.500	0.757	-0.255	1.719	126.701	2.363	126.699
3.6	-24.419	0.128	-24.930	0.571	-0.308	1.017	-23.509	1.757	-23.506
3.7	-17.327	0.152	-16.729	0.424	-0.350	0.523	-115.326	1.297	-115.324
3.8	-12.147	0.163	-10.974	0.310	-0.378	0.185	-167.342	0.951	-167.346
3.9	-8.392	0.166	-6.978	0.222	-0.393	-0.041	-192.735	0.697	-192.740
4.0	-5.692	0.163	-4.239	0.156	-0.395	-0.186	-200.741	0.513	-200.747
4.1	-3.770	0.155	-2.390	0.107	-0.389	-0.272	-197.781	0.385	-197.783
4.2	-2.415	0.145	-1.164	0.071	-0.373	-0.318	-188.246	0.298	-188.248
4.3	-1.472	0.134	-0.371	0.044	-0.355	-0.336	-175.110	0.242	-175.107
4.4	-0.825	0.123	0.124	0.026	-0.333	-0.336	-160.330	0.207	-160.325
4.5	-0.389	0.111	0.419	0.013	-0.308	-0.324	-145.167	0.185	-145.163
4.6	-0.103	0.100	0.578	0.004	-0.282	-0.305	-130.404	0.170	-130.403
4.7	0.079	0.090	0.650	-0.002	-0.258	-0.282	-116.498	0.157	-116.497
4.8	0.189	0.080	0.666	-0.006	-0.234	-0.259	-103.683	0.146	-103.682
5.0	0.277	0.064	0.609	-0.009	-0.189	-0.212	-81.609	0.125	-81.613
5.2	0.276	0.050	0.510	-0.009	-0.153	-0.170	-64.073	0.104	-64.075
5.4	0.242	0.040	0.409	-0.008	-0.122	-0.136	-50.404	0.084	-50.403
5.6	0.199	0.032	0.321	-0.007	-0.097	-0.108	-39.836	0.067	-39.833
5.9	0.141	0.022	0.221	-0.005	-0.070	-0.077	-28.321	0.048	-28.320
6.2	0.098	0.016	0.153	-0.004	-0.050	-0.055	-20.458	0.035	-20.460
6.5	0.068	0.012	0.107	-0.003	-0.036	-0.040	-15.023	0.025	-15.025
7.0	0.037	0.007	0.061	-0.002	-0.022	-0.024	-9.294	0.015	-9.292
7.5	0.021	0.005	0.037	-0.001	-0.014	-0.015	-5.970	0.010	-5.969
8.0	0.013	0.003	0.023	-0.001	-0.009	-0.010	-3.960	0.007	-3.961
9.0	0.005	0.001	0.010	0.000	-0.004	-0.005	-1.889	0.003	-1.889
10.0	0.002	0.001	0.005	0.000	-0.002	-0.002	-0.982	0.002	-0.982
12.0	0.001	0.000	0.001	0.000	-0.001	-0.001	-0.319	0.001	-0.320
15.0	0.000	0.000	0.000	0.000	0.000	0.000	-0.082	0.000	-0.082

atoms of small or medium atomic weight, scalar relativistic methods such as the mass-velocity-Darwin (MVD) approach introduced by Cowan and Griffin,<sup>44</sup> the DKH method,<sup>22,23</sup> and the direct perturbation theory (DPT), developed by Rutkowski,<sup>45</sup> Kutzelnigg,<sup>46</sup> and Klopper,<sup>47</sup> cover most of the relativistic contributions to the electronic energy. This conclusion is supported by the fact that the state-of-the-art *ab initio* pair potentials for neon and for argon,<sup>6,7,9</sup> which were developed using the MVD approach for the relativistic corrections, were employed to derive highly accurate thermophysical property values in almost perfect agreement with the best experimental data.<sup>48</sup> To the best of our knowledge, no detailed study on the relativistic contributions to the krypton-krypton interaction energy is available in the literature. However, for Xe<sub>2</sub> and heavier elements, investigations on the effects beyond the scalar relativistic level were carried out. Runeberg and Pyykkö<sup>49</sup> calculated the spin-(own)-orbit contribution to the Xe<sub>2</sub> dissociation energy to be as large as 8.1 K, but this value might be affected by the incompleteness of the basis set and by the limitations of the utilized CISD approach as pointed out by Kullie and Saue.<sup>50</sup> The recent study of Shee *et al.*<sup>51</sup> incorporates a comparison of the CCSD(T) results for the dissociation energy of heavy noble gas dimers obtained from calculations with and without consideration of the Gaunt term, which accounts for the interaction between the spin of one electron with the magnetic moment of another one. For Xe<sub>2</sub>, the CBS-extrapolated difference attributed to the Gaunt effect was reported to be 0.69 K, i.e., the well depth is increased if the Gaunt term is considered. Even though Waldrop *et al.*<sup>19</sup> tested the relativistic effects for the krypton dimer at the two-component level using the Breit-Pauli hamiltonian<sup>52</sup> and stated that contributions beyond the scalar relativistic DKH approximation are negligible, we followed the analysis for xenon and included full four-component computations and the Gaunt term in our investigation.

The relativistic correction to the interaction energy of the krypton dimer was calculated as a sum of four terms,

$$V_{\text{rel}} = V_{\text{DPT2/FC,CBS}} + V_{\text{DPT2,IFC-FC}} + V_{4\text{cDC-DPT2}} + V_{\text{Gaunt}}. \quad (3)$$

The first contribution,  $V_{\text{DPT2/FC,CBS}}$ , was computed using the second-order direct perturbation theory (DPT2) at the CCSD(T)/FC level of theory as implemented in the CFOUR program.<sup>32</sup> For  $R = 4.0 \text{ \AA}$ , we obtained values of  $V_{\text{DPT2/FC}}^{\text{dawCVQZ}+(3321)} = -4.433 \text{ K}$  and  $V_{\text{DPT2/FC}}^{\text{dawCV5Z}+(3321)} = -4.338 \text{ K}$ . Following Waldrop *et al.*,<sup>19</sup> the results were extrapolated to the CBS limit according to Eq. (1) giving a value of  $V_{\text{DPT2/FC,CBS}}^{\text{dawCV5Z}+(3321)} = -4.239 \text{ K}$ . The second term in Eq. (3) corrects the first one for core-core and core-valence correlation effects;  $V_{\text{DPT2,IFC-FC}}$  was calculated as the difference between the DPT2 relativistic corrections obtained for the IFC and for the FC approximations (see Sec. II D) using the dawCVQZ+(3321) basis set. The additional effect of the core electrons was found to be rather small, with the value for  $R = 4.0 \text{ \AA}$  being  $V_{\text{DPT2,IFC-FC}}^{\text{dawCVQZ}+(3321)} = 0.156 \text{ K}$ . Summing up the first two terms in Eq. (3) results in a scalar relativistic correction to the interaction energy of  $-4.083 \text{ K}$  for the test geometry. This value is in close agreement with the one

reported by Waldrop *et al.* ( $-4.046 \text{ K}$ ), which was obtained from all-electron DKH computations with fully uncontracted aVXZ basis sets.

The third term in Eq. (3) accounts mainly for the spin-(own)-orbit contribution to the interaction energy. We evaluated this correction as the difference between the results for the relativistic correction determined from FC four-component Dirac-Coulomb (4cDC) computations (with explicit calculation of the two-electron (SS|SS) integrals over the small component as implemented in the DIRAC program<sup>36</sup>) and corresponding values computed with the DPT2/CCSD(T)/FC approach. Fully uncontracted aVXZ+(3321) basis sets were applied resulting in corrections to the interaction energy of  $V_{4\text{cDC-DPT2}}^{\text{unc-aVDZ}+(3321)} = -0.389 \text{ K}$  and  $V_{4\text{cDC-DPT2}}^{\text{unc-aVTZ}+(3321)} = -0.395 \text{ K}$  for  $R = 4.0 \text{ \AA}$ . The unextrapolated values obtained for the triple-zeta basis set were used as the  $V_{4\text{cDC-DPT2}}$  reference values. As shown in Table IV, this correction is negative for all distances  $R$  with a slight local minimum around the well of the total pair potential.

The last term in Eq. (3) accounts for the difference between the Dirac-Coulomb and the Dirac-Coulomb-Gaunt hamiltonians used for the four-component calculations. For this correction, both theoretical levels (DC and DCG) were treated within the molecular mean-field approximation (see Ref. 53 for further details), since this is at the moment the only way to combine DCG computations with coupled-cluster methods. A similar approach using the exact two-component molecular mean-field hamiltonian with added Gaunt term was employed by Shee *et al.*<sup>51</sup> for the heavier noble gas dimers. For the krypton dimer at  $R = 4.0 \text{ \AA}$ , differences of  $V_{\text{Gaunt}}^{\text{unc-aVDZ}+(3321)} = -0.127 \text{ K}$  and  $V_{\text{Gaunt}}^{\text{unc-aVTZ}+(3321)} = -0.186 \text{ K}$  were found. Again, the results for the larger basis set were chosen as final values for Eq. (3). The Gaunt correction to the interaction energy is positive for small distances  $R$ , shows a zero-crossing close to  $R = 3.9 \text{ \AA}$ , and has a minimum of  $-0.336 \text{ K}$  at about  $R = 4.4 \text{ \AA}$ . The sum of both four-component corrections amounts to  $-0.581 \text{ K}$  for the test geometry resulting in a total relativistic correction of  $-4.664 \text{ K}$ .

## F. Uncertainty budget

The combined uncertainty of the *ab initio* interaction energies was determined as the square root of the sum of the squared uncertainties resulting from the individual contributions in accordance with the standard procedure for the evaluation of measurement uncertainties. Waldrop *et al.*<sup>19</sup> computed each of the uncertainty contributions as the difference between the CBS-extrapolated values and the corresponding values obtained for the higher basis set used in the two-point extrapolation. Patkowski and Szalewicz,<sup>9</sup> who utilized this approach for some of the correction terms to the interaction energy of Ar<sub>2</sub>, reported that the resulting uncertainties corresponded to rather conservative estimates, which we interpret as expanded uncertainties with coverage factor  $k = 2$ . In this paper, we decided to estimate standard uncertainties (i.e.,  $k = 1$ ) for the CBS-extrapolated contributions to the interaction energy by taking half of the



extrapolation intervals. Thus,

$$\begin{aligned} u(V_{\text{corr}}) &= \frac{1}{2} \left( V_{\text{corr,CBS}}^{\text{taV6Z}+(44332)} - V_{\text{corr}}^{\text{taV6Z}+(44332)} \right), \\ u(V_{\text{T-(T)}}) &= \frac{1}{2} \left( V_{\text{T-(T),CBS}}^{\text{daV5Z}+(3321)} - V_{\text{T-(T)}}^{\text{daV5Z}+(3321)} \right), \\ u(V_{\text{(Q)-T}}) &= \frac{1}{2} \left( V_{\text{(Q)-T,CBS}}^{\text{aVQZ}} - V_{\text{(Q)-T}}^{\text{aVQZ}} \right), \\ u(V_{\text{IFC-FC}}) &= \frac{1}{2} \left( V_{\text{IFC-FC,CBS}}^{\text{dawCV5Z}+(3321)} - V_{\text{IFC-FC}}^{\text{dawCV5Z}+(3321)} \right), \\ u(V_{\text{DPT2/FC,CBS}}) &= \frac{1}{2} \left( V_{\text{DPT2/FC,CBS}}^{\text{dawCV5Z}+(3321)} - V_{\text{DPT2/FC}}^{\text{dawCV5Z}+(3321)} \right). \end{aligned}$$

Further uncertainty contributions were computed as

$$\begin{aligned} u(V_{\text{SCF}}) &= V_{\text{SCF}}^{\text{taV6Z}+(44332)} - V_{\text{SCF}}^{\text{taV5Z}+(44332)}, \\ u(V_{\text{Q-(Q)}}) &= \frac{1}{2} V_{\text{Q-(Q)}}^{\text{aVDZ}+(3321)}, \\ u(V_{\text{AE-IFC}}) &= V_{\text{AE-IFC}}^{\text{unc-aVQZ}+(3321)} - V_{\text{AE-IFC}}^{\text{unc-aVTZ}+(3321)}, \\ u(V_{\text{4cDC-DPT2}}) &= V_{\text{4cDC-DPT2}}^{\text{unc-aVTZ}+(3321)} - V_{\text{4cDC-DPT2}}^{\text{unc-aVDZ}+(3321)}, \\ u(V_{\text{Gaunt}}) &= V_{\text{Gaunt}}^{\text{unc-aVTZ}+(3321)} - V_{\text{Gaunt}}^{\text{unc-aVDZ}+(3321)}. \end{aligned}$$

The correction term  $V_{\text{DPT2,IFC-FC}}$  is rather small and was therefore not considered in the uncertainty evaluation. For contributions beyond the CCSDTQ level of theory, we allocated a small uncertainty of  $u(V_{\text{post-CCSDTQ}}) = \frac{1}{2}u(V_{\text{Q-(Q)}})$ , which is about ten times larger than the computed value of  $V_{\text{(P)-Q}}$  for  $R = 4 \text{ \AA}$ . The described propagation of uncertainty results in a combined standard uncertainty of  $u_c = 0.513 \text{ K}$  for the test geometry with a total interaction energy of  $V = -200.741 \text{ K}$ . The values of the total interaction energy,  $V^{\text{tot}}$ , and of the combined standard uncertainty,  $u_c(V^{\text{tot}})$ , for all 36 distances  $R$  are listed in Table IV, whereas the underlying *ab initio* results can be found in the supplementary material.<sup>58</sup>

### G. Nonadditive three-body interactions

Accurate predictions of thermophysical properties for thermodynamic states beyond the low-density regime are relying on the knowledge of many-body interactions, which are dominated by nonadditive three-body interactions  $\Delta V_3$ . Our studies on argon<sup>54,55</sup> have shown that the simple ATM model, reflecting the nonadditive triple-dipole interactions, is a very robust model with regard to the derived third and higher-order virial coefficients. Even though some features of the ATM model deviate fundamentally from the true *ab initio* nonadditive three-body potential, especially for triplet configurations with small interatomic distances, a large amount of error cancellation within the ATM model can be assumed to be the reason for this agreement. However, Pospisil *et al.*<sup>56</sup> reported rather large contributions to the third virial coefficients of krypton arising from dispersion terms beyond the triple-dipole approximation. Therefore, we chose to use not only the pure ATM model but also the so-called extended ATM (EATM) nonadditive potential for the computation of the third virial coefficient and the discussion of the corresponding uncertainty. The EATM model as employed by Schwerdtfeger

*et al.* (see Ref. 57 and references therein) is given by

$$\Delta V_{3,\text{EATM}} = f_\theta \left[ C_{\text{ATM}} R_g^{-9} + \exp(-\alpha R_s) \sum_{n=0}^5 A_{2n} R_g^{2n} \right], \quad (4)$$

where  $f_\theta = 1 + 3 \cos\theta_i \cos\theta_j \cos\theta_k$ ,  $R_g = (R_{ij}R_{ik}R_{jk})^{1/3}$ ,  $R_s = R_{ij} + R_{ik} + R_{jk}$ , and  $R_{ij}$ ,  $R_{ik}$ ,  $R_{jk}$  are the interatomic distances in the triangle formed by the three atoms  $i$ ,  $j$ ,  $k$  with the corresponding interior angles  $\theta_i$ ,  $\theta_j$ ,  $\theta_k$ . The nonadditivity parameter  $C_{\text{ATM}}$  was chosen to be  $C_{\text{ATM}} = 1.61525 \times 10^6 \text{ K \AA}^9$  ( $=1572 \text{ a.u.}$ ), obtained from the dipole oscillator strength distribution (DOSD) of Kumar and Meath.<sup>58</sup> If the parameters  $A_{2n}$  are set to zero, the standard ATM potential results. Following Schwerdtfeger *et al.*, the parameters of the EATM potential were determined from *ab initio* nonadditive three-body interaction energies computed for a series of equilateral triangles. We chose 11 distances  $R$  ranging from  $2.5 \text{ \AA}$  to  $6 \text{ \AA}$  and calculated  $\Delta V_3(R)$  as the sum of four contributions,

$$\begin{aligned} \Delta V_3 &= \Delta V_{3,\text{CCSD(T),FC}}^{\text{aVQZ}+(3321)} + \Delta V_{3,\text{T-(T)}}^{\text{aVDZ}+(3321)} \\ &\quad + \Delta V_{3,\text{IFC-FC}}^{\text{awCVDZ}+(3321)} + \Delta V_{3,\text{DPT2/IFC}}^{\text{awCVDZ}+(3321)}, \quad (5) \end{aligned}$$

representing the CCSD(T)/FC prediction and corrections for higher coupled-cluster terms up to CCSDT, for core-core and core-valence correlation, as well as for relativistic effects at the DPT2 level. In contrast to the findings for the  $\text{Kr}_2$  interaction energy, where the (Q)-T and T-(T) contributions almost cancel, the (Q)-T correction is considerably smaller than the T-(T) correction for the nonadditive three-body interaction and has therefore been neglected. Each of the contributions was calculated using the nonadditive three-body version of the supermolecular approach, which reduces for equilateral triangles to

$$\Delta V_3 = E_{ijk} - 3 E_{ij} + 3 E_i, \quad (6)$$

where  $E_{ijk}$ ,  $E_{ij}$ , and  $E_i$  are the energies obtained for the trimer as well as for the involved dimers and monomers, with the latter two being calculated in the full basis set of the trimer according to the counterpoise correction. The bond functions were placed in the center of the triplet. The parameters  $\alpha = 1.378382 \text{ \AA}^{-1}$ ,  $A_0 = -0.3081304 \times 10^8 \text{ K}$ ,  $A_2 = -0.3519442 \times 10^8 \text{ K \AA}^{-2}$ ,  $A_4 = 0.4928052 \times 10^7 \text{ K \AA}^{-4}$ ,  $A_6 = -0.2182411 \times 10^6 \text{ K \AA}^{-6}$ , and  $A_8 = 0.3430880 \times 10^4 \text{ K \AA}^{-8}$  were determined by means of a least-squares procedure;  $A_{10}$  was not needed and therefore set to zero. The *ab initio* results for  $\Delta V_3$  are summarized along with the values for the ATM potential and the fitted EATM function in Table V. Due to the relatively small basis sets, the correction terms can only be regarded as estimates. As expected, relativistic effects (column 5 of Table V) were observed to have a considerable influence on the interaction energy for small and medium distances, whereas the correction for the full treatment of triple excitations (column 3 of Table V) is of relative importance for larger  $R$ . Additional test calculations for  $\Delta V_3$  at  $R = 8 \text{ \AA}$  and at  $R = 10 \text{ \AA}$  are in close agreement with the long-range asymptotic behavior of the ATM model characterized by deviations within  $\pm 3\%$ , thus confirming the applied quantum-chemical approach according to Eq. (5). The trend to negative nonadditive three-body interactions  $\Delta V_3$  at short interatomic distances in contrast to

TABLE V. Nonadditive three-body interaction energies for equilateral krypton trimers according to Eqs. (5) and (6) in Kelvin as well as corresponding EATM and ATM values as a function of the distance  $R$ .

$R / \text{Å}$	$\Delta V_{3,\text{CCSD(T),FC}}^{\text{aVQZ+(3321)}}$	$\Delta V_{3,\text{T-(T)}}^{\text{aVDZ+(3321)}}$	$\Delta V_{3,\text{IFC-FC}}^{\text{awCVDZ+(3321)}}$	$\Delta V_{3,\text{DPT2/IFC}}^{\text{awCVDZ+(3321)}}$	$\Delta V_3$	$\Delta V_{3,\text{EATM}}$	$\Delta V_{3,\text{ATM}}$
2.50	-4720.589	16.285	114.444	439.074	-4150.785	-4152.011	582.214
2.75	-1531.363	9.343	44.269	169.296	-1308.456	-1309.770	246.916
3.00	-449.064	5.586	16.024	61.696	-365.757	-365.789	112.837
3.25	-109.473	3.260	5.348	21.027	-79.838	-79.760	54.903
3.50	-14.868	1.831	1.597	6.595	-4.846	-4.846	28.179
3.75	5.834	1.001	0.396	1.852	9.083	9.080	15.145
4.00	7.306	0.544	0.054	0.428	8.333	8.345	8.472
4.25	5.221	0.300	-0.017	0.066	5.570	5.563	4.910
4.50	3.288	0.170	-0.025	-0.017	3.416	3.414	2.935
5.00	1.246	0.061	-0.012	-0.016	1.279	1.281	1.137
6.00	0.230	0.010	-0.002	-0.002	0.237	0.236	0.220

the ATM model is a typical behavior (see, for example, Refs. 57 and 54), which is mainly due to exchange interactions. We note that the fitted EATM model fails to predict the nonadditive three-body interaction energy for triplet configurations with geometries that differ distinctly from equilateral shape. In fact, test calculations for linear configurations showed that the EATM model is much closer to the ATM model than to the respective *ab initio* results, as the short-range damping behavior in the case of linear configurations is drastically underestimated by the exponential term in Eq. (4). However, linear and similar configurations can be expected to be of minor importance from a thermodynamic perspective, since they are associated with smaller Boltzmann weights compared to those for the corresponding equilateral configurations. Therefore, the EATM model is regarded as an improvement over the ATM potential.

### III. ANALYTICAL POTENTIAL FUNCTION AND VIBRATIONAL SPECTRUM OF THE KRYPTON ATOM PAIR

The total interaction energies were obtained as

$$V^{\text{tot}} = V_{\text{SCF}} + V_{\text{corr}} + V_{\text{post-CCSD(T)}} + V_{\text{AE-FC}} + V_{\text{rel}}. \quad (7)$$

A modified Tang-Toennies type analytical function<sup>59</sup> was used to represent the 36 interaction energies as a function of the interatomic distance  $R$ ,

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

The parameters  $A$ ,  $a_1$ ,  $a_2$ ,  $a_{-1}$ ,  $b$ ,  $C_6$ ,  $C_8$ , and  $C_{10}$  were determined within a least-squares procedure with the further dispersion coefficients being determined simultaneously according to the approximate recursion formula<sup>59</sup>

$$C_{2n} = C_{2n-6} \left( \frac{C_{2n-2}}{C_{2n-4}} \right)^3, \quad n \geq 6. \quad (9)$$

Following Patkowski *et al.*<sup>60</sup> and our own study on argon,<sup>11</sup> Eq. (8) was replaced for  $R < 0.3R_e$  by a simple exponential function in order to avoid any unphysical extrapolation to the

extremely repulsive region,

$$V_{\text{sr}}(R) = \frac{\tilde{A}}{R} \exp(-\tilde{a}R), \quad R < 0.3R_e, \quad (10)$$

where the parameters  $\tilde{A}$  and  $\tilde{a}$  were determined in such a way that the potential and its first derivative are in agreement with the Tang-Toennies function at  $R = 0.3R_e$ . Table VI contains all parameters along with the well depth  $\varepsilon/k_B$  and the minimum distance  $R_e$ , whereas Table IV shows the calculated total *ab initio* interaction energies and the corresponding values for the analytical function. Furthermore, we chose pair potentials for different levels of the relativistic correction, one for the nonrelativistic limit of the potential  $V^{\text{nonrel}} = V^{\text{tot}} - V_{\text{rel}}$ , and the other one for  $V^{\text{DPT2}} = V^{\text{tot}} - V_{\text{Gaunt}} - V_{4\text{cDC-DPT2}}$ , and determined the respective potential parameters. In accordance with the procedure employed by Waldrop *et al.*,<sup>19</sup> additional potential parameter sets were obtained from fits to the

TABLE VI. Parameters of the *ab initio* pair potential,  $V^{\text{tot}}$ , and characteristic parameters of the pair potentials of Aziz and Slaman,<sup>13</sup> of Slavíček *et al.*,<sup>16</sup> and of Waldrop *et al.*<sup>19</sup> as well as a literature value for the  $C_6$  coefficient by Kumar and Meath.<sup>58</sup> Note that not all figures displayed are significant, but are given to avoid round-off errors.

	Unit	Value	Literature values	Reference
$A$	K	$0.320071\,1798 \times 10^8$		
$a_1$	$\text{Å}^{-1}$	$-0.243\,056\,5544 \times 10^1$		
$a_2$	$\text{Å}^{-2}$	$-0.143\,553\,6209$		
$a_{-1}$	$\text{Å}$	$-0.453\,227\,3868$		
$b$	$\text{Å}^{-1}$	$0.278\,634\,4368 \times 10^1$		
$C_6$	$\text{K Å}^6$	$0.899\,220\,9265 \times 10^6$	$0.898\,65 \times 10^6$ $0.879\,17 \times 10^6$	58 19
$C_8$	$\text{K Å}^8$	$0.731\,671\,3603 \times 10^7$		
$C_{10}$	$\text{K Å}^{10}$	$0.783\,548\,851\,1 \times 10^8$		
$\tilde{A}$	$\text{K Å}$	$0.826\,800\,5465 \times 10^7$		
$\tilde{a}$	$\text{Å}^{-1}$	$0.168\,249\,3666 \times 10^1$		
$\varepsilon/k_B$	K	200.8753	201.3 194.37 201.52	13 16 19
$R_e$	$\text{Å}$	4.015802	4.011 4.037 4.0135	13 16 19

total interaction energies modified by adding or subtracting the calculated combined standard uncertainties, i.e.,  $V^{U1} = V^{\text{tot}} + u_c$  and  $V^{U2} = V^{\text{tot}} - u_c$ . Moreover, we determined two additional curves,  $V^{U3}$  and  $V^{U4}$ , by modulating the uncertainty function for the repulsive region ( $R \leq 4$  Å) by  $\pm \cos[\pi(R - 2.2 \text{ Å})/(4.0 \text{ Å} - 2.2 \text{ Å})]$ . Finally, a “refitted” pair potential  $V^{\text{refit-W}}$  based on the total interaction energies presented by Waldrop *et al.* was derived using the more flexible analytical function of the present work.

The  $C_6$  coefficient obtained for our pair potential is in perfect agreement with the value obtained from the DOSD of Kumar and Meath<sup>58</sup> with a deviation of less than 0.1%, whereas the value for the potential of Waldrop *et al.*<sup>19</sup> deviates by about  $-2.2\%$ . This is partly due to the limited flexibility of the long range part of their analytical function, where only dispersion terms with  $R^{-6}$  and  $R^{-8}$  dependencies were used. The refitted potential,  $V^{\text{refit-W}}$ , is characterized by  $C_6 = 0.8910 \times 10^6 \text{ K Å}^6$ , corresponding to a deviation of  $-0.9\%$ . The combined standard uncertainty of the well depth for the potential of the present work, following from  $V^{U1}$  and  $V^{U2}$ , is  $u_c(\varepsilon/k_B) = 0.51 \text{ K}$ . The distance of the minimum amounts to  $R_\varepsilon = (4.0158 \pm 0.0014) \text{ Å}$ . The well depth of the empirical pair potential of Aziz and Slaman<sup>13</sup> agrees with that of our potential within the estimated uncertainty, whereas  $R_\varepsilon$  deviates by about  $-0.005 \text{ Å}$ . The *ab initio* pair potential of Slavíček *et al.*<sup>16</sup> is characterized by distinctly larger differences due to the use of an effective-core potential to account for relativistic effects and to the neglect of higher correlation contributions. Our result for  $\varepsilon/k_B$  agrees with the value of  $\varepsilon/k_B = 201.52 \text{ K}$  reported for the *ab initio* pair potential of Waldrop *et al.* within its estimated uncertainty of  $u_c(\varepsilon/k_B) = 1.1 \text{ K}$ . However, the difference of  $0.64 \text{ K}$  between the  $\varepsilon/k_B$  values is slightly larger than our estimate for the uncertainty. For the refitted potential,  $V^{\text{refit-W}}$ , the deviation increases to  $0.81 \text{ K}$ . The nonrelativistic and DPT2-level potentials are characterized by  $\varepsilon/k_B = 196.71 \text{ K}$  and  $\varepsilon/k_B = 200.27 \text{ K}$ , respectively. The latter value is somewhat outside the combined standard uncertainty estimated for our total potential, and it deviates by  $-1.25 \text{ K}$  from the well depth of the potential of Waldrop *et al.*, which was developed using a similar scalar relativistic correction. This difference emerges mainly from the differing quantum-chemical results for  $V_{\text{corr}}$

and  $V_{\text{post-CCSD(T)}}$  and is cancelled partly when the additional relativistic corrections are added to  $V^{\text{DPT2}}$ .

As a first test of the quality of the new pair potential, the frequencies of vibrational transitions for the electronic ground state of the krypton dimer were computed by solving the one-dimensional radial Schrödinger equation. We used the LEVEL program (version 7.7) developed by Le Roy<sup>62</sup> and employed the relative atomic mass of 83.9115 for the most abundant krypton isotope  $^{84}\text{Kr}$ . The uncertainties for the vibrational spacings were obtained as the maximum deviations of the values resulting for  $V^{U1}$  through  $V^{U4}$  from the reference values for  $V^{\text{tot}}$ . The results are contained along with experimental data and corresponding values for the other pair potentials in Table VII. The theoretical results for the *ab initio* potentials of this work and of Waldrop *et al.*<sup>19</sup> are in agreement with the experimental data of Tanaka *et al.*<sup>61</sup> within the relatively large measurement uncertainties, except for the  $5 \rightarrow 4$  transition, as Waldrop *et al.* have already discussed. The results for the *ab initio* potential of Waldrop *et al.* are in perfect agreement with the values for  $V^{\text{tot}}$  within the mutual estimated uncertainties. Note that the uncertainty limits for the present potential are distinctly smaller than those for the potential of Waldrop *et al.* In contrast, the results for the empirical pair potential of Aziz and Slaman<sup>13</sup> disagree for half of the transitions with the values for  $V^{\text{tot}}$  considering our estimated uncertainty range. Furthermore, two transitions for  $^{86}\text{Kr}_2$  (relative atomic mass of 85.9106) were computed using  $V^{\text{tot}}$  to compare with the experimental data of LaRocque *et al.*<sup>63</sup> Our results of  $21.2291 \text{ cm}^{-1}$  for  $1 \rightarrow 0$  and of  $19.109 \text{ cm}^{-1}$  for  $2 \rightarrow 1$  differ from the experimental values by  $0.054 \text{ cm}^{-1}$  and  $0.016 \text{ cm}^{-1}$ , respectively, whereas the results for the pair potential of Waldrop *et al.* are characterized by slightly larger deviations of  $0.065 \text{ cm}^{-1}$  and  $0.038 \text{ cm}^{-1}$ .

#### IV. VIRIAL COEFFICIENTS

The virial equation of state characterizes the non-ideal thermodynamic behavior of gases and supercritical fluids. It is given for the pressure,  $p$ , as a series expansion in the (molar) density,  $\rho_m$ ,

$$\frac{p}{\rho_m RT} = 1 + B_2(T)\rho_m + B_3(T)\rho_m^2 + \dots, \quad (11)$$

TABLE VII. Vibrational spacings  $\Delta G_{v+1/2}$  for the vibrational transitions  $v+1 \rightarrow v$  of the electronic ground state of  $^{84}\text{Kr}_2$  in  $\text{cm}^{-1}$  for  $V^{\text{tot}}$ ,  $V^{\text{nonrel}}$ , and  $V^{\text{DPT2}}$  as well as for the pair potentials from the literature of Aziz and Slaman,<sup>13</sup> of Slavíček *et al.*,<sup>16</sup> and of Waldrop *et al.*<sup>19</sup> Experimental data are those of Tanaka *et al.*<sup>61</sup>

$v$	$\Delta G_{v+1/2} / \text{cm}^{-1}$						
	This work, $V^{\text{tot}}$	This work, $V^{\text{nonrel}}$	This work, $V^{\text{DPT2}}$	Ref. 13	Ref. 16	Ref. 19	Experiment
0	$21.455 \pm 0.033$	21.212	21.434	21.41	20.96	$21.466 \pm 0.081$	$21.56 \pm 0.54$
1	$19.285 \pm 0.029$	19.039	19.260	19.30	18.79	$19.307 \pm 0.077$	$19.09 \pm 0.57$
2	$17.133 \pm 0.026$	16.886	17.105	17.20	16.65	$17.166 \pm 0.073$	$16.76 \pm 0.60$
3	$15.010 \pm 0.026$	14.762	14.979	15.11	14.54	$15.053 \pm 0.069$	$14.76 \pm 0.75$
4	$12.930 \pm 0.028$	12.682	12.897	13.02	12.49	$12.980 \pm 0.065$	$12.23 \pm 0.51$
5	$10.911 \pm 0.029$	10.666	10.875	10.97	10.51	$10.963 \pm 0.062$	$10.49 \pm 0.50$
6	$8.976 \pm 0.030$	8.738	8.938	9.01	8.63	$9.026 \pm 0.060$	$8.92 \pm 0.44$
7	$7.154 \pm 0.030$	6.929	7.117	7.17	6.87	$7.199 \pm 0.063$	$6.92 \pm 0.63$
8	$5.481 \pm 0.029$	5.274	5.445	5.49	5.26	$5.517 \pm 0.064$	$5.54 \pm 0.30$

where  $T$  is the temperature and  $R$  is the molar gas constant. A main advantage of this approach is the direct relation of the virial coefficients  $B_2(T), B_3(T), \dots$  to intermolecular interactions (see, for example, Ref. 64). Therefore, comparison of results for virial coefficients computed from *ab initio* interaction potentials with experimentally determined values is a valuable check for the quantum-chemical approaches used in the development of potential functions.

A semi-classical approach was employed for the calculation of both the second and the third virial coefficients,  $B_2(T)$  and  $B_3(T)$ , where each quantity was obtained as a sum of the classical contribution and quantum corrections. As in the case of argon,<sup>11</sup> the computation of  $B_2(T)$  included first-through third-order quantum corrections,

$$B_2(T) = B_2^{\text{cl}}(T) + \lambda B_2^{\text{qm},1}(T) + \lambda^2 B_2^{\text{qm},2}(T) + \lambda^3 B_2^{\text{qm},3}(T), \quad (12)$$

where  $\lambda = \hbar^2 \beta / 12m$ ,  $\beta = (k_B T)^{-1}$ ,  $m = 83.798 u$  is the average atomic mass of naturally occurring krypton, and  $\hbar$  is Planck's constant divided by  $2\pi$ . The explicit formulae for the individual contributions  $B_2^{\text{cl}}(T), \dots, B_2^{\text{qm},3}(T)$  are summarized, for example, in Ref. 10 and are therefore not repeated here. The third virial coefficient of krypton was calculated as a sum of four terms,

$$B_3(T) = B_{3,\text{add}}^{\text{cl}}(T) + B_{3,\text{nadd}}^{\text{cl}}(T) + \lambda [B_{3,\text{add}}^{\text{qm}}(T) + B_{3,\text{nadd}}^{\text{qm}}(T)]. \quad (13)$$

Here,  $B_{3,\text{add}}^{\text{cl}}(T)$  refers to the third virial coefficient in the pairwise additive approximation, whereas  $B_{3,\text{nadd}}^{\text{cl}}$  is the correction for nonadditive three-body interactions. First-order quantum corrections were considered for both the additive term ( $\lambda B_{3,\text{add}}^{\text{qm}}$ ) and the nonadditive correction ( $\lambda B_{3,\text{nadd}}^{\text{qm}}$ ), the latter one being calculated using the approximation that the second derivatives of the nonadditive three-body potential can be neglected compared to the second derivatives of the pair potential.<sup>65</sup> Explicit expressions for the contributions to the third virial coefficient can be found elsewhere.<sup>56,64,65</sup> All integrals for the computation of the second and third virial coefficients were solved by means of standard numerical integration methods. The results for  $B_2(T)$  and  $B_3(T)$  are converged to within  $\pm 0.001 \text{ cm}^3 \text{ mol}^{-1}$  and  $\pm 0.1 \text{ cm}^6 \text{ mol}^{-2}$ , respectively.

## A. Second virial coefficient

The second virial coefficient of krypton was computed for the temperature range from 70 to 5000 K employing the pair potential functions  $V^{\text{tot}}$ ,  $V^{\text{nonrel}}$ , and  $V^{\text{DPT2}}$  as well as the pair potentials of Aziz and Slaman,<sup>13</sup> Slaviček *et al.*,<sup>16</sup> and Waldrop *et al.*<sup>19</sup> The standard uncertainties of the computed  $B_2$  values for  $V^{\text{tot}}$  were estimated from the calculations for the potentials  $V^{\text{tot}}$ ,  $V^{\text{U1}}$ , and  $V^{\text{U2}}$  as

$$u(B_2) = \max \{ B_2(V^{\text{U1}}) - B_2(V^{\text{tot}}), B_2(V^{\text{U2}}) - B_2(V^{\text{tot}}) \}. \quad (14)$$

As expected, due to the large atomic weight of krypton, the values of the summed quantum corrections,  $B_2 - B_2^{\text{cl}}$ , are quite small, ranging from  $6.4 \text{ cm}^3 \text{ mol}^{-1}$  at  $T = 70 \text{ K}$  to less than  $0.1 \text{ cm}^3 \text{ mol}^{-1}$  at ambient temperature and above.

The large number of experimental data for the second virial coefficient of krypton was carefully reviewed by Dymond *et al.*<sup>66</sup> However, Aziz and Slaman<sup>13</sup> have already stated that the literature data showed a large scatter and were therefore not considered by them as primary data for the development of their pair potential. Unfortunately, neither  $pVT$  measurements with a highly accurate two-sinker densimeter nor speed-of-sound measurements using a spherical resonator have been performed for krypton until today. Therefore, experimental data with estimated uncertainties of less than  $0.3 \text{ cm}^3 \text{ mol}^{-1}$  are scarce.

We compare our calculated values of the second virial coefficient with sets of measured data<sup>67–75</sup> selected from the compilation of Dymond *et al.* and with values computed for the other pair potentials in Fig. 1. Isothermal  $pVT$  data were measured by Beattie *et al.*<sup>67</sup> and by Trappeniers *et al.*,<sup>69</sup> yielding second virial coefficient values with an estimated uncertainty of  $1 \text{ cm}^3 \text{ mol}^{-1}$ . For the comparison, we chose the set of  $B_2$  values from Ref. 69 that was obtained from cubic fits of low-density  $pVT$  data. Whalley and Schneider<sup>68</sup> as well as Dillard *et al.*<sup>73</sup> employed the Burnett method, resulting in  $B_2$  values with stated uncertainties of  $0.3\text{--}0.6 \text{ cm}^3 \text{ mol}^{-1}$  and  $0.1 \text{ cm}^3 \text{ mol}^{-1}$ , respectively. For the low-temperature region, we compare with the data of Byrne *et al.*,<sup>70</sup> who performed relative measurements with helium as reference gas and reported uncertainty estimates of  $(1.5\text{--}3.0) \text{ cm}^3 \text{ mol}^{-1}$ . The group of Schramm<sup>74,75</sup> employed compression and temperature changing methods with nitrogen as the reference gas and estimated the uncertainty to be  $2 \text{ cm}^3 \text{ mol}^{-1}$ . The  $B_2$  values of Pollard<sup>71</sup> and of Santafe *et al.*<sup>72</sup> are characterized by uncertainty estimates of  $2\text{--}3 \text{ cm}^3 \text{ mol}^{-1}$ .

One additional set of  $B_2$  values was considered in this work. It was derived from  $pVT$  data measured by Evers *et al.*<sup>76</sup> with the single-sinker densimeter that is part of their combined viscometer-densimeter apparatus. For each of the two available isotherms at 298.15 K and 348.15 K, the data points for the three lowest densities were omitted in the evaluation, since the measurements at lower density using this type of densimeter are characterized by an increasing uncertainty.<sup>76</sup> The remaining values for the compressibility factors were fitted using quadratic polynomials,  $p/\rho_m RT = 1 + B_2(T)\rho_m + B_3(T)\rho_m^2$ , resulting in  $B_2 = -50.41 \text{ cm}^3 \text{ mol}^{-1}$  and  $B_3 = 2241 \text{ cm}^6 \text{ mol}^{-2}$  at  $T = 298.15 \text{ K}$  as well as  $B_2 = -33.58 \text{ cm}^3 \text{ mol}^{-1}$  and  $B_3 = 1753 \text{ cm}^6 \text{ mol}^{-2}$  at  $T = 348.15 \text{ K}$ . A simple estimation for the uncertainty of these virial coefficients was made by adding or removing one or two data points from each of the isotherms. Thus, uncertainties of  $0.9 \text{ cm}^3 \text{ mol}^{-1}$  and  $340 \text{ cm}^6 \text{ mol}^{-2}$  at  $T = 298.15 \text{ K}$  and  $0.4 \text{ cm}^3 \text{ mol}^{-1}$  and  $230 \text{ cm}^6 \text{ mol}^{-2}$  at  $T = 348.15 \text{ K}$  were obtained.

Fig. 1 shows that the calculated low-temperature values for the second virial coefficient of krypton are in agreement with most of the experimental data from Refs. 70 and 71 within their uncertainties at temperatures above 170 K. However, at still lower temperatures, deviations of up to  $16 \text{ cm}^3 \text{ mol}^{-1}$  were found, as already discussed by Dham *et al.*<sup>14</sup> in their review on empirical pair potentials for krypton. Other experimental data sets in the range from 110 to 170 K (see Ref. 66) show similar trends with decreasing temperature.



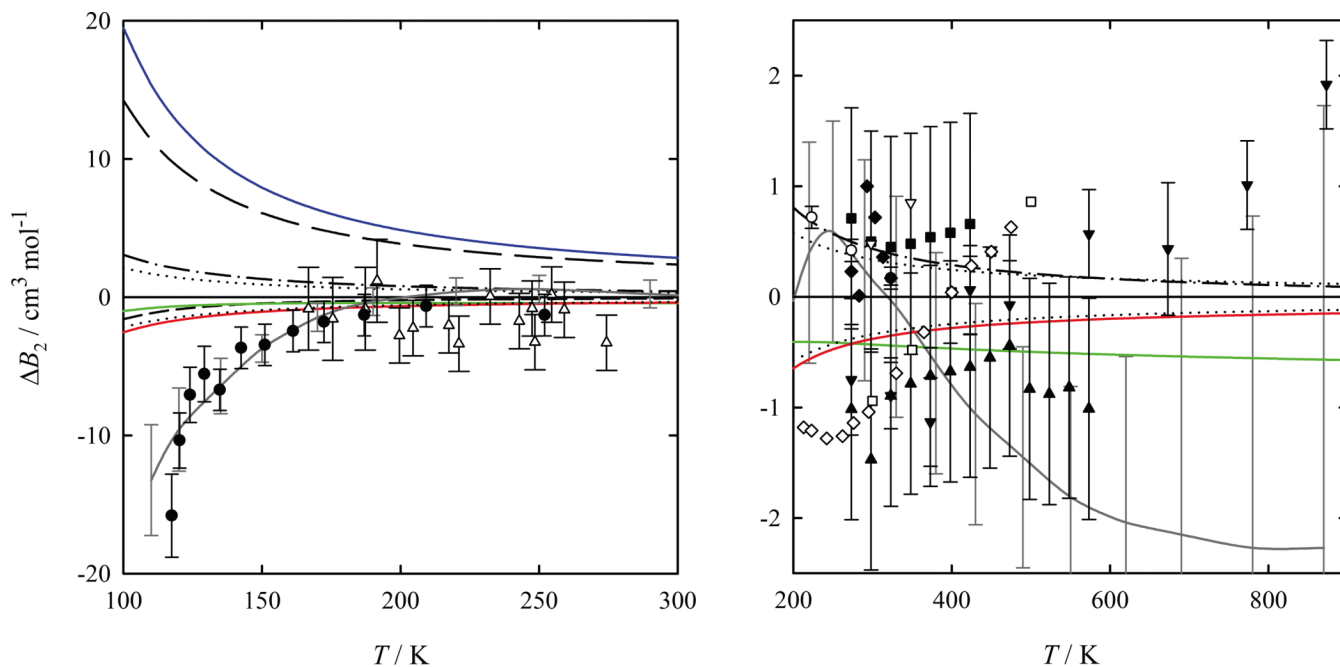


FIG. 1. Absolute deviations of experimentally based and of theoretically calculated values for the second virial coefficient of krypton from those calculated using the theoretical pair potential  $V^{\text{tot}}$ . Experimental data:  $\blacktriangle$ , Beattie *et al.*;<sup>67</sup>  $\blacktriangledown$ , Whalley and Schneider;<sup>68</sup>  $\blacksquare$ , Trappeniers *et al.*;<sup>69</sup>  $\bullet$ , Byrne *et al.*;<sup>70</sup>  $\triangle$ , Pollard;<sup>71</sup>  $\blacklozenge$ , Santafe *et al.*;<sup>72</sup>  $\circ$ , Dillard *et al.*;<sup>73</sup>  $\square$ , Perez *et al.*;<sup>74</sup>  $\diamond$ , Schmiedel *et al.*;<sup>75</sup>  $\nabla$ , Evers *et al.*<sup>76</sup> Experimental correlation: (gray line), Dymond *et al.*<sup>66</sup> Calculated values: (green line), empirical potential of Aziz and Slaman;<sup>13</sup> (blue line), *ab initio* potential of Slavíček *et al.*;<sup>16</sup> (red line), *ab initio* potential of Waldrop *et al.*;<sup>19</sup> — — —, this work using  $V^{\text{nonrel}}$ ; — · — · —, this work using  $V^{\text{DPT}2}$ ; — — —, classical calculation using  $V^{\text{tot}}$ ; ·······, range of the standard uncertainty. The uncertainty estimates for Refs. 72 and 74–76 were omitted for clarity.

At medium and high temperatures, the  $B_2$  values computed for  $V^{\text{tot}}$  agree with the data of Beattie *et al.*,<sup>67</sup> of Trappeniers *et al.*,<sup>69</sup> of Santafe *et al.*,<sup>72</sup> and of Schramm and co-workers<sup>74,75</sup> within their rather large experimental uncertainty estimates. The deviations from the theoretically calculated  $B_2$  values for some of the data of Whalley and Schneider,<sup>68</sup> of Dillard *et al.*,<sup>73</sup> and of Evers *et al.*<sup>76</sup> exceed the mutual estimated uncertainties. At temperatures from 180 to 400 K, the values computed for  $V^{\text{tot}}$  are consistent with the correlation of Dymond *et al.*<sup>66</sup> to within  $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$ , whereas the deviations from the calculated values increase to about  $-13 \text{ cm}^3 \text{ mol}^{-1}$  at 110 K and to  $-2.3 \text{ cm}^3 \text{ mol}^{-1}$  at 870 K. We note that the uncertainties of most of the experimental data exceed those inferred for the theoretically computed values.

The almost perfect agreement of our calculated values for  $V^{\text{tot}}$  with those for the empirical potential of Aziz and Slaman<sup>13</sup> implies that the  $pVT$  measurements for  $T < 170 \text{ K}$  might have been affected by adsorption. The values computed for  $V^{\text{nonrel}}$  and for the potential of Slavíček *et al.*<sup>16</sup> show considerable positive deviations from the values for  $V^{\text{tot}}$ , illustrated in Fig. 1 for the low-temperature region. This is due to the distinctly smaller well depths of these potentials. At ambient and lower temperatures, the deviations for  $V^{\text{DPT}2}$  and for the recent *ab initio* potential of Waldrop *et al.*<sup>19</sup> are slightly larger than our computed standard uncertainties  $u(B_2)$  in accordance with the corresponding deviations for  $\varepsilon/k_B$ . However, the experimental data for the second virial coefficient are not accurate enough to discriminate between the pair potentials of Waldrop *et al.* and that of the present work. The results for  $B_2(T)$  are listed in the supplementary material.<sup>38</sup>

## B. Third virial coefficient

The third virial coefficient of krypton was calculated for three levels of theory, the purely pairwise-additive approximation using  $V^{\text{tot}}$ , the  $V^{\text{tot}}$ +ATM combination, and the  $V^{\text{tot}}$ +EATM combination (see Sec. II G). The first-order quantum correction to the pairwise-additive approximation is positive for all temperatures, whereas the quantum correction to the nonadditive contribution is negative. Both corrections are within  $\pm 1 \text{ cm}^6 \text{ mol}^{-2}$  at ambient temperature and increase in magnitude to  $\lambda B_{3,\text{add}}^{\text{qm}} = 325 \text{ cm}^6 \text{ mol}^{-2}$  and  $\lambda B_{3,\text{nadd}}^{\text{qm}} = -62 \text{ cm}^6 \text{ mol}^{-2}$  at 120 K. This is still small compared to the total value at that temperature,  $B_3^{\text{EATM}} = -12\,818 \text{ cm}^6 \text{ mol}^{-2}$ . The values of the combined standard uncertainty for the EATM model were computed as the square root of the sum of three squared uncertainty contributions that were obtained as follows. The standard uncertainty for  $B_{3,\text{add}}^{\text{cl}}$  was determined from the values for the purely additive approach as

$$u^{\text{I}}(B_3) = \max \left\{ \left| B_{3,\text{add}}^{\text{cl}}(V^{\text{U}1}) - B_{3,\text{add}}^{\text{cl}}(V^{\text{tot}}) \right|, \left| B_{3,\text{add}}^{\text{cl}}(V^{\text{U}2}) - B_{3,\text{add}}^{\text{cl}}(V^{\text{tot}}) \right| \right\}. \quad (15)$$

The uncertainty of the pair potential gives also rise to an uncertainty for the nonadditive correction,  $B_{3,\text{nadd}}^{\text{cl}}$ , whose standard uncertainty,  $u^{\text{II}}(B_3)$ , was computed following Eq. (15) with  $B_{3,\text{add}}^{\text{cl}}$  being replaced by the nonadditive correction  $B_{3,\text{nadd}}^{\text{cl}}$ . The third contribution to the uncertainty budget,  $u^{\text{III}}(B_3)$ , which arises from the uncertainty of the nonadditive three-body potential, was conservatively estimated to be three times the absolute value of the difference between  $B_{3,\text{nadd}}^{\text{cl}}$  computed for the ATM and EATM models. Contributions

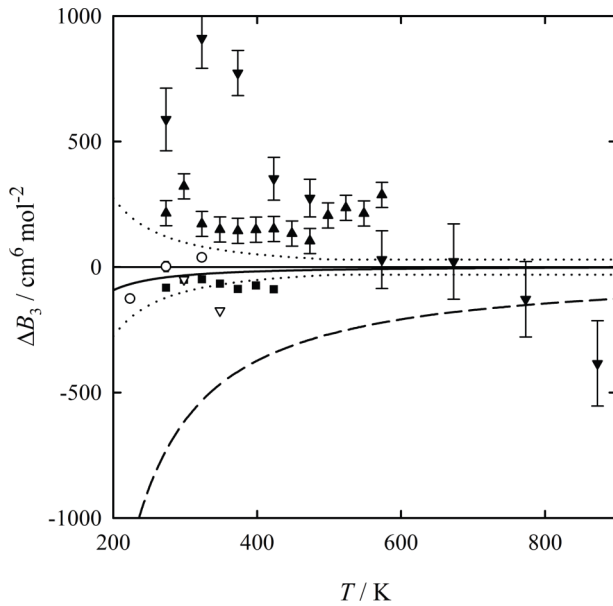


FIG. 2. Absolute deviations of experimentally based and of theoretically calculated values for the third virial coefficient of krypton from those calculated using the theoretical pair potential  $V^{\text{tot}}$  in conjunction with the EATM potential. Experimental data: ▲, Beattie *et al.*,<sup>67</sup> ▼, Whalley and Schneider,<sup>68</sup> ■, Trappeniers *et al.*,<sup>69</sup> ○, Dillard *et al.*,<sup>73</sup> ▽, Evers *et al.*<sup>76</sup> Calculated values: —, pairwise additive approximation; —, ATM potential; ·····, range of the standard uncertainty. The uncertainty estimates of Trappeniers *et al.*<sup>69</sup> and of Dillard *et al.*<sup>73</sup> were omitted for clarity.

from the quantum corrections were not considered due to their small magnitude (see above). Finally, a value of  $u_c(B_3) = 30 \text{ cm}^6 \text{ mol}^{-2}$  was chosen as the lower bound to the combined standard uncertainty.

Only in four of the studies on the  $pVT$  behavior of krypton discussed in Sec. IV A, the measurements were evaluated to infer second and third virial coefficients (Refs. 67–69 and 73). The corresponding uncertainty estimates are  $50 \text{ cm}^6 \text{ mol}^{-2}$  for Ref. 67,  $75\text{--}170 \text{ cm}^6 \text{ mol}^{-2}$  for Ref. 68,  $500\text{--}1000 \text{ cm}^6 \text{ mol}^{-2}$  for Ref. 69, and  $10\text{--}20 \text{ cm}^6 \text{ mol}^{-2}$  for Ref. 73. As described in Sec. IV A, two additional values for  $B_3$  were obtained from the experimental data of Evers *et al.*<sup>76</sup>

Fig. 2 illustrates that the differences between the third virial coefficients calculated for the EATM and ATM nonadditive three-body potentials are distinctly smaller than those between the different experimental data sets. Nevertheless, the comparison with the values for the pairwise-additive approximation confirms that nonadditive three-body interactions are necessary for an accurate prediction of  $B_3$ . The

theoretical values for the EATM model are in close agreement with the data sets of Trappeniers *et al.*,<sup>69</sup> Dillard *et al.*,<sup>73</sup> and Evers *et al.*,<sup>76</sup> whereas the data of Beattie *et al.*<sup>67</sup> and most of the data of Whalley and Schneider<sup>68</sup> exhibit deviations larger than the corresponding uncertainty estimates. For most of the data sets, it can be observed that positive deviations for the third virial coefficient go along with negative deviations for the second virial coefficient, and vice versa. This interrelation is attributed to inadequate procedures for the determination of virial coefficient values from the experimental  $pVT$  data using the virial equation of state. The same conclusion can be drawn from the assessment of theoretical values and experimental data for the second and third virial coefficients of argon<sup>11,54</sup> and nitrogen.<sup>77</sup> The results for the third virial coefficient of krypton are listed in the supplementary material.<sup>38</sup>

## V. TRANSPORT PROPERTIES

### A. Theory

Transport properties of dilute monatomic gases can be calculated with high accuracy from *ab initio* pair potential functions via solving the Boltzmann equation.<sup>48</sup> The traditional approach involves the computation of temperature-dependent collision integrals  $\Omega^{(l,m)}$  as introduced by Chapman and Cowling,<sup>78</sup> which can be done either classically or quantum-mechanically. Explicit expressions for the calculation of the transport properties in terms of collision integrals are available in the literature (see Ref. 78 for the second-order approximations, Ref. 79 for fifth-order approximations to the pure-component viscosity and thermal conductivity, and Ref. 80 for the higher-order approximations to the mass and thermal diffusion coefficients).

We use an equivalent approach based on the generalized kinetic theory of molecular gases and gaseous mixtures<sup>81</sup> for consistency with our studies on transport properties of polyatomic substances (see, for example, Refs. 82–84). Curtiss<sup>85</sup> worked out a solution to the generalized Boltzmann equation for rigid linear molecules, and later Dickinson *et al.*<sup>86</sup> extended this method to asymmetric-top molecules. The temperature-dependent generalized cross sections  $\sigma'$  and  $\sigma''$ , which appear in the solution and characterize the binary collision dynamics, can be simplified for particles interacting through spherically symmetrical pair potentials, as already indicated by Curtiss and by Chen *et al.*<sup>87</sup> For collisions between particles of species  $\alpha$  and  $\beta$ , including the case  $\alpha = \beta$ , one obtains

$$\sigma' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{\alpha\beta} = \frac{2\pi^{3/2}}{(2p+1)^{1/2}} \sum_{l, n, n'} (2l+1)^{1/2} I_{\ln n'; ps ps'}^{(0)}(y_\alpha, y_\beta) \sum_{i_1=0}^n \sum_{i_2=0}^{n'} (-1)^{i_1+i_2} L(n, l, i_1) L(n', l, i_2) \times \int_0^\infty \exp(-\gamma^2) \gamma^{3+2(l+i_1+i_2)} \int_0^\infty [1 - P_l(\cos \chi)] b db dy \quad (16)$$

and

$$\sigma'' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{\alpha\beta} = \frac{2\pi^{3/2}}{(2p+1)^{1/2}} \sum_{lnn'} (-1)^l (2l+1)^{1/2} I_{lnn';psps'}^{(0)}(y_\alpha, y_\beta) \left( \frac{y_\alpha}{y_\beta} \right)^{(4n'+2l-2s'-p)} \sum_{i_1=0}^n \sum_{i_2=0}^{n'} (-1)^{i_1+i_2} L(n, l, i_1) L(n', l, i_2) \times \int_0^\infty \exp(-\gamma^2) \gamma^{3+2(l+i_1+i_2)} \int_0^\infty [1 - P_l(\cos \chi)] b db d\gamma. \quad (17)$$

We refer to Ref. 86 for the definitions of the mass ratios  $y_\alpha$  and  $y_\beta$ , the reduced relative velocity  $\gamma$ , and the expansion coefficients  $L$  of the normalized associated Laguerre polynomials. Chen *et al.*<sup>87</sup> as well as Curtiss<sup>85</sup> gave the details for the coefficients  $I$  arising from the transformation between the center-of-mass and laboratory reference frames. The impact parameter  $b$  and the deflection angle  $\chi$  are the same as in the original formulation<sup>78</sup> for  $\Omega^{(l,m)}$ , and  $P_l$  are  $l$ th-order Legendre polynomials. The ranges of the summation indices  $n$ ,  $n'$ , and  $l$  were given by Chen *et al.*<sup>87</sup> Moreover,  $l > 0$  since contributions for  $l = 0$  vanish. Chen *et al.* also indicated how the collision integrals  $\Omega^{(l,m)}$  are introduced into Eqs. (16) and (17). It can be shown that

$$\int_0^\infty \exp(-\gamma^2) \gamma^{3+2(l+i_1+i_2)} \int_0^\infty [1 - P_l(\cos \chi)] b db d\gamma = \sum_{t=0}^{\lfloor (l-1)/2 \rfloor} \frac{(-1)^t}{2^l} \binom{l}{t} \binom{2l-2t}{l} \frac{2}{\pi \langle v \rangle_{\alpha\beta}} \Omega_{\alpha\beta}^{(l-2t, l+i_1+i_2)}, \quad (18)$$

where  $\langle v \rangle_{\alpha\beta} = (8k_B T / \pi \mu_{\alpha\beta})^{1/2}$  is the average relative thermal speed and  $\mu_{\alpha\beta}$  is the reduced mass; the notation  $\lfloor \dots \rfloor$  indicates rounding down to the next integer.

Each transport coefficient can be obtained from the solution  $X$  to a system of linear equations, where the cross sections enter as coefficients. For pure gases, only the summed cross sections  $\Xi \left( \begin{matrix} ps \\ ps' \end{matrix} \right) \equiv \sigma' \left( \begin{matrix} ps \\ ps' \end{matrix} \right) + \sigma'' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)$  are needed for viscosity and thermal conductivity within this formalism. The viscosity  $\eta$  of a pure monatomic gas results from a system of linear equations with  $p = 2$ ,

$$\sum_{s'=0}^\infty \Xi \left( \begin{matrix} 2s \\ 2s' \end{matrix} \right) X^{2s'} = \frac{\delta_{s0} C^{20}}{\langle v \rangle}, \quad s = 0, 1, \dots, \infty, \quad (19)$$

as

$$\eta = \frac{1}{2} k_B T C^{20} X^{20}, \quad (20)$$

where  $\delta_{ij}$  is the Kronecker delta,  $\langle v \rangle$  is the pure-component average relative thermal speed, and  $C^{20} = \sqrt{2}$ . The thermal conductivity  $\lambda$  results from a system of linear equations with  $p = 1$ ,

$$\sum_{s'=1}^\infty \Xi \left( \begin{matrix} 1s \\ 1s' \end{matrix} \right) X^{1s'} = \frac{\delta_{s1} C^{11}}{\langle v \rangle}, \quad s = 1, \dots, \infty, \quad (21)$$

as

$$\lambda = k_B C^{11} X^{11}, \quad (22)$$

where  $C^{11} = (5k_B T / 2m)^{1/2}$ . Equations (21) and (22) can be deduced from Eqs. (15) and (17) of Ref. 84 by omitting the internal degrees of freedom.

For self-diffusion, the following system of linear equations is to be solved:

$$\sum_{s'=0}^\infty \sigma' \left( \begin{matrix} 1s \\ 1s' \end{matrix} \right) X^{1s'} = \frac{\delta_{s0} C^{10}}{\langle v \rangle}, \quad s = 0, 1, \dots, \infty, \quad (23)$$

where  $C^{10} = (k_B T / m)^{1/2}$ . The product of molar density and self-diffusion coefficient,  $\rho_m D_{\text{self}}$ , is then obtained as

$$\rho_m D_{\text{self}} = \frac{C^{10} X^{10}}{N_A}, \quad (24)$$

where  $N_A$  is Avogadro's constant. Equations (23) and (24) can be derived straightforwardly from the formalism for binary mixtures of molecular gases, which is given, for example, in Ref. 82. To this end, a mixture of two monatomic components A and B that satisfies  $m_A = m_B$ ,  $\sigma' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{AA} = \sigma' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{AB} = \sigma' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{BB}$  and  $\sigma'' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{AA} = \sigma'' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{AB} = \sigma'' \left( \begin{matrix} ps \\ ps' \end{matrix} \right)_{BB}$  is assumed.

Solving the systems of linear equations for  $s, s' \leq n$  leads to the  $(n+1)$ th-order approximations for viscosity and self-diffusion and the  $n$ th-order approximation for thermal conductivity. In the present work, we computed  $\eta$ ,  $\lambda$ , and  $\rho_m D_{\text{self}}$  for  $n = 4$ . All necessary collision integrals were calculated using a modified version of the program code developed by O'Hara and Smith.<sup>88,89</sup>

The standard uncertainties of the transport properties  $z = \eta, \lambda, \rho_m D_{\text{self}}$  were determined from the differences between the results obtained for the pair potentials  $V^{U1}, \dots, V^{U4}$  and those for  $V^{\text{tot}}$  as

$$u(z) = \max \{ |z(V^{U1}) - z(V^{\text{tot}})|, \dots, |z(V^{U4}) - z(V^{\text{tot}})| \}. \quad (25)$$

Quantum effects on the transport properties are usually neglected for krypton due to the large atomic mass and difficulties in the quantum-mechanical treatment. However, we inferred from calculations of Munn *et al.*<sup>90</sup> for the Lennard-Jones (12-6) potential that the quantum effects on the transport properties of krypton can be as large as the standard uncertainties that result from the uncertainty of our pair potential. Therefore, the combined standard uncertainties for the transport properties were estimated as  $u_c(z) = 1.5 u(z)$ . All results obtained for the pair potential  $V^{\text{tot}}$  are listed along with the corresponding uncertainty estimates in the supplementary material.<sup>38</sup>

## B. Viscosity

The theoretical calculations for the viscosity correspond to the limit of zero density. Of course, experiments in this limit are not possible, and most measurements were often carried out at about atmospheric pressure. To infer values at zero density, the experimental data have to be corrected using values of the initial density dependence,  $\lim_{\rho \rightarrow 0} (\partial \eta / \partial \rho)_T / \eta$ , where  $\rho$  is the mass density. Unfortunately, values of this density coefficient characterized by low uncertainty are only available at room temperature, see, for example, Table 2 in Ref. 4. To perform the correction at any temperature, the Rainwater-Friend theory<sup>91</sup> is to be applied. For that purpose, we used the original potential parameter ratios of Rainwater and Friend<sup>91</sup> and the Lennard-Jones (12-6) length and energy parameters for krypton of Hanley *et al.*<sup>92</sup> This procedure differs from that applied by Waldrop *et al.*,<sup>19</sup> who used the revised parameter ratios of Bich and Vogel,<sup>93</sup> which were optimized for a wider range of substances (including organic vapors) and are therefore less suitable for noble gases (see also Fig. 5.3 of Ref. 94). The standard uncertainty resulting from this correction can be of the order of 0.05%–0.3% depending on the magnitude of the correction itself, which can amount to 2%–3% near the normal boiling point, decreasing to 0.1%–0.2% at higher temperatures. Fortunately, some experiments in the literature were performed as isothermal series of measurements as a function of density, so that zero-density data could be obtained by extrapolation to this limit.

The comparison of the experimental data available in the literature with the theoretically computed values of the present

work has been restricted to data of low uncertainty and data extending over wide temperature ranges. The measurements of our group performed on krypton<sup>95</sup> in 1984 were re-evaluated for this work, because the all-quartz oscillating-disk viscometer used for the relative measurements was originally calibrated with an experimentally based reference value for the zero-density viscosity of argon at room temperature recommended by Kestin *et al.*<sup>96</sup> in 1972, which is now outdated. For the re-calibration of the viscometer and the re-evaluation of the measured viscosity data for krypton, a viscosity value at room temperature theoretically calculated for argon by Vogel *et al.*<sup>11</sup> was used. In the comparison, we also include unpublished data from two series of measurements performed by Strehlow for his Ph.D. thesis<sup>97</sup> at the University of Rostock in 1987. These measurements were re-evaluated in the same manner.

In Fig. 3(a), selected experimental data close to room temperature are compared with the theoretically calculated viscosity values for krypton. The most recent datum at 298.15 K by Berg and Burton<sup>4</sup> (with an uncertainty of 0.04%), measured by means of a capillary viscometer calibrated with a viscosity value for helium obtained from an extremely accurate interatomic potential,<sup>3</sup> deviates from our theoretical value by less than +0.01%. In 2012, Berg and Moldover<sup>98</sup> critically reviewed reliable viscosity data from the literature resulting from measurements for krypton near 298.15 K and corrected them to zero density. They used viscosity ratios related to different gases and anchored them to the aforementioned theoretical viscosity value of helium. Their recommended viscosity value for krypton at 298.15 K is only 0.11% higher

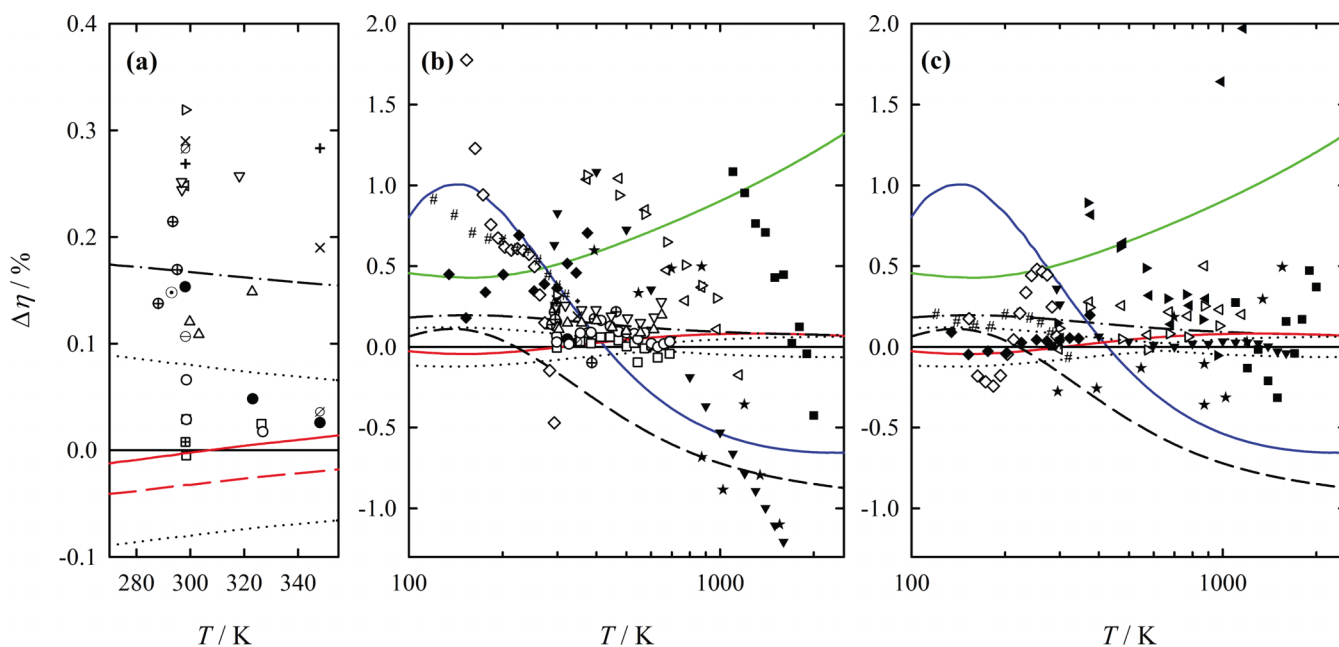


FIG. 3. Relative deviations of experimental and theoretical values for the viscosity of dilute krypton from those calculated using the pair potential  $V^{\text{tot}}$ . Experimental data:  $\circ$ , Kestin and Leidenfrost;<sup>101</sup>  $\bullet$ , Trappeniens *et al.*;<sup>99</sup>  $\blacklozenge$ , Clarke and Smith;<sup>105</sup>  $\nabla$ , Dawe and Smith;<sup>108</sup>  $\triangleleft$ , Kalelkar and Kestin;<sup>103</sup>  $\blacksquare$ , Goldblatt *et al.*;<sup>110</sup>  $\triangleright$ , Kestin *et al.*;<sup>96</sup>  $\star$ , Maitland and Smith;<sup>109</sup>  $\#$ , Gough *et al.*;<sup>106</sup>  $\oplus$ , Timrot and Traktueva;<sup>104</sup>  $\emptyset$ , van den Berg and Trappeniens;<sup>100</sup>  $\diamond$ , Lukin *et al.*;<sup>107</sup>  $\triangle$ , Vogel, 1st series;<sup>95</sup>  $\nabla$ , Vogel, 2nd series;<sup>95</sup>  $\square$ , Strehlow, 1st series;<sup>97</sup>  $\circ$ , Strehlow, 2nd series;<sup>97</sup>  $+$ , Wilhelm and Vogel;<sup>102</sup>  $\times$ , Evers *et al.*;<sup>76</sup>  $\boxplus$ , Berg and Burton;<sup>4</sup>  $\ominus$ , Berg and Moldover.<sup>98</sup> Calculated values: (green line), empirical potential of Aziz and Slaman;<sup>13</sup> (blue line), *ab initio* potential of Slavíček *et al.*;<sup>16</sup> (red line), *ab initio* potential of Waldrop *et al.*;<sup>19</sup> (dashed red line), refitted *ab initio* potential of Waldrop *et al.*;<sup>19</sup> — —, this work using  $V^{\text{nonrel}}$ ; — · —, this work using  $V^{\text{DPT}2}$ ; · · · · ·, range of the standard uncertainty. The data shown in panel (c) were obtained from the zero-density values by multiplying each of them by  $\eta_{\text{ab initio, Ar}} / \eta_{\text{exp, Ar}}$ . Two further sets of values are shown in panel (c) that were obtained from recalibration with helium as reference gas:  $\blacktriangleleft$ , Kalelkar and Kestin;<sup>103</sup>  $\blacktriangleright$ , Kestin *et al.*<sup>96</sup>



than the theoretical value. The measurements of Trappeniers *et al.*<sup>99</sup> and those of van den Berg and Trappeniers<sup>100</sup> were performed with capillary viscometers using an absolute mode of operation, while those of Evers *et al.*<sup>76</sup> were carried out using an absolute rotating-cylinder viscometer. The deviations of the results of Trappeniers *et al.* decrease between 298.15 K and 348.15 K from +0.15% to +0.03%, those of van den Berg and Trappeniers drop from +0.28% to +0.04%, and those of Evers *et al.* decrease from +0.29% to +0.20%. The measurements of Kestin and Leidenfrost<sup>101</sup> with an oscillating-disk viscometer and those of Wilhelm and Vogel<sup>102</sup> with a vibrating-wire viscometer used a relative mode of operation, in which the viscometers were calibrated with reference values that are now outdated. This leads to an experimental datum differing by +0.15% for the measurement of Kestin and Leidenfrost, whereas the data of Wilhelm and Vogel are about 0.28% too high. The measurements of Kalelkar and Kestin,<sup>103</sup> of Kestin *et al.*,<sup>96</sup> and of Timrot and Traktueva<sup>104</sup> were performed with oscillating-disk viscometers using a relative mode of operation. For the calibration of the viscometers, the data of Kestin and Leidenfrost<sup>101</sup> were applied as reference, so that the results should be expected to deviate by about +0.2%. With +0.25% for Kalelkar and Kestin, +0.32% for Kestin *et al.*, and +(0.14%–0.21%) for Timrot and Traktueva, this is approximately the case. Finally, the deviations of the re-evaluated data of the first series of Vogel<sup>95</sup> amount to about +0.12% and those of the second series to +0.25%, whereas the deviations of the unpublished re-evaluated data of Strehlow<sup>97</sup> near room temperature do not exceed +0.07%.

Figure 3(b) focuses on the deviations of experimental data covering large temperature ranges. The re-evaluated data of our group are again included in Fig. 3(b) since the data of Vogel and of Strehlow extend up to 650 K and 690 K, respectively. The temperature dependence of the experimental data measured with the quartz-glass oscillating-disk viscometer is fully consistent with that of the theoretical values. Up to the highest temperatures, the deviations correspond approximately to those already discussed for room temperature. The only other data for which the deviations are characterized by a negligible temperature dependence over the investigated temperature range are those of Timrot and Traktueva.<sup>104</sup> The deviations amount from –0.10% to +0.22% at temperatures up to 463 K.

Further data sets that extend to high or low temperatures, but whose temperature dependencies differ from that of the theoretically calculated values, are also included in Fig. 3(b). Three data sets measured with capillary viscometers are available down to 120 K. The data of Clarke and Smith<sup>105</sup> and of Gough *et al.*<sup>106</sup> were obtained in a relative mode of operation, in which the deviations near room temperature are about +0.4%. The experimental datum of Lukin *et al.*<sup>107</sup> at room temperature, which was determined with a relaxation method, deviates from the theoretical value by –0.47%. The deviations of the data of Gough *et al.* and of Lukin *et al.* increase with decreasing temperature up to +0.9% at 120 K and +1.8% at 153 K, respectively, whereas the deviations of the data of Clarke and Smith vary between +0.18% and +0.71% down to 134 K. Furthermore, we consider three other data sets obtained with capillary

viscometers in a relative mode of operation at temperatures up to 1600 K or even 2000 K. The data of Dawe and Smith<sup>108</sup> and of Maitland and Smith<sup>109</sup> are characterized around room temperature by deviations of about +0.8% and +0.3%, respectively, while Goldblatt *et al.*<sup>110</sup> did not perform measurements below 1100 K. The deviations of the three data sets vary in the investigated temperature ranges from +1.1% to –1.2% (Dawe and Smith), +0.6% to –1.1% (Maitland and Smith), and +1.1% to –0.4% (Goldblatt *et al.*). The uncertainties of the four data sets of Smith and co-workers<sup>105,106,108,109</sup> were estimated by the authors to be of the order of 0.5% at room temperature, increasing to 1.0% and 1.5% at the lowest and highest temperatures, respectively, whereas the uncertainties for the data of Goldblatt *et al.* and Lukin *et al.* were assumed to be 0.6% and 0.3%, respectively, which is certainly too optimistic. Kestin *et al.*<sup>96</sup> assumed for the best estimates of their measured results an uncertainty at room temperature of 0.1%, rising to 0.15% at 473 K, 0.2% at 773 K, and 0.3% at 973 K. The causes for the differences at room temperature have already been discussed above. As can be seen in Fig. 3(b), the deviations of the data of Refs. 96 and 103 from the theoretical values reach +1.1% at 373 K and subsequently decrease with increasing temperature. Thus, the deviations exceed the claimed uncertainties considerably, which is consistent with the findings for other gases such as argon<sup>11</sup> and nitrogen.<sup>77</sup>

The situation that the temperature dependencies of the deviations and consequently of the experimental viscosity data are not consistent with that of the theoretically calculated values is quite disappointing. The data sets from the corresponding eight papers do not enable to check the reliability of the theoretical calculations. To test the quality of these data sets, we followed partly a proposal by Berg and collaborators<sup>98,111,112</sup> to use reliably measured ratios between the viscosity of the investigated gas and that of a reference gas, for which helium should be selected due to the extraordinarily low uncertainty of the computed viscosity values for helium.<sup>2,3</sup> An analogous procedure was used by Waldrop *et al.*<sup>19</sup> for the improvement of the literature viscosity data. In doing so, Waldrop *et al.* recommended to compute revised viscosity data for krypton,  $\eta_{\text{rev,Kr}}$ , by multiplying the original experimental data,  $\eta_{\text{exp,Kr}}$ , with values of a viscosity ratio,  $\eta_{\text{ab initio,ref}}/\eta_{\text{exp,ref}}$ , following from experimental data for a reference gas determined in the same paper and corresponding calculated *ab initio* viscosity values. Waldrop *et al.* re-evaluated the original krypton data by means of *ab initio* viscosity values for helium (from Ref. 3), argon (privately communicated by Mehl), or nitrogen (from Ref. 77). This procedure corresponds to a calibration of the respective viscometer at each measuring temperature assuming that the conditions are the same for the measurements on krypton and on the reference gas.

The approach of Waldrop *et al.* using helium is inappropriate for the experimental data of Kestin and co-workers.<sup>96,103</sup> For their re-evaluation, we used, in a first step, the viscosity values for helium of Cencek *et al.*<sup>3</sup> The resulting deviations of the experimental data for krypton of Kestin and co-workers are illustrated in Fig. 3(c). In comparison with the deviations for the original data, plotted in Fig. 3(b), the

discrepancies between most of the experimental data and the theoretical values are approximately the same, whereas at the highest temperatures for the measurements of Kalelkar and Kestin, they are even larger (up to +2.0%). The reason that no reduction of the deviations occurs for the data of Kestin and co-workers is a temperature measurement error due to the thermocouples employed in their high-temperature oscillating-disk viscometer. This error, which was discussed extensively by Vogel,<sup>113,114</sup> is dependent on the thermal conductivity of the investigated gas; it increases with decreasing thermal conductivity. Since the thermal conductivity of helium is very high compared with that of nitrogen, argon, and krypton (about 6, 9, and 16 times larger), the error is very small for helium. Hence, in a second step, we chose argon as the reference gas. The resulting deviations, also shown in Fig. 3(c), do not exceed  $\pm 0.3\%$ , apart from one data point of Kalelkar and Kestin at 873 K.

We re-evaluated all data sets, whenever possible, using helium and argon data from the same paper as reference gas data. In the case of Goldblatt *et al.*, it was necessary to use data of a preceding paper by Guevara *et al.*<sup>115</sup> The deviations for the high-temperature data sets of Dawe and Smith,<sup>108</sup> Goldblatt *et al.*,<sup>110</sup> and Maitland and Smith,<sup>109</sup> re-evaluated with helium, revealed no improvement, but rather a deterioration, whereas the deviations of the low-temperature data sets of Gough *et al.*<sup>106</sup> and Lukin *et al.*<sup>107</sup> decrease considerably using helium for the re-evaluation. Figure 3(c) shows that all krypton data re-evaluated by means of argon data deviate within  $\pm 0.5\%$  from the theoretical viscosity values, with the majority of the deviations being within  $\pm 0.3\%$ . Since these deviations are always smaller than for helium, argon should be preferred to helium as reference gas for such a re-evaluation.

In Fig. 3, we also show the comparison of computed viscosity values for the *ab initio* pair potential of the present work,  $V^{\text{tot}}$ , with those for other pair potentials. The values obtained for the empirical potential of Aziz and Slaman<sup>13</sup> deviate by about +0.5% from the values for  $V^{\text{tot}}$  at  $T < 300$  K, whereas the deviations increase to 1.7% at 5000 K. For the potential of Slavíček *et al.*,<sup>16</sup> the computed viscosity values show positive deviations of up to 1.0% at low temperatures and negative deviations of up to  $-0.65\%$  at temperatures above 1000 K. The nonrelativistic potential of the present work,  $V^{\text{nonrel}}$ , results in  $\eta$  values that are in close agreement with those for  $V^{\text{tot}}$  at  $T < 300$  K, but exhibit deviations of up to  $-0.92\%$  at 5000 K. This reflects the incompleteness of the nonrelativistic pair potential especially in the short-range region. Remarkably, the viscosity values for the recent *ab initio* potential of Waldrop *et al.*<sup>19</sup> are in agreement with the results for  $V^{\text{tot}}$  within  $\pm 0.08\%$  for the entire temperature range. Moreover, the theoretical values for both potentials deviate by no more than 0.02% from the experimental datum of Berg and Burton<sup>4</sup> at room temperature, whereas the refitted version of the potential of Waldrop *et al.* differs by  $-0.04\%$ . The deviations for the pair potential  $V^{\text{DPT}2}$ , which is almost equivalent to the potential of Waldrop *et al.* with respect to the treatment of the relativistic correction, are somewhat larger (up to 0.2%). Therefore, it may be concluded that the perfect agreement of the results for the potential of Waldrop *et al.* with those for  $V^{\text{tot}}$  is at least partly due to a cancellation of errors

resulting from several quantum-chemical contributions to the interaction energies and from the limited accuracy of the fitted analytical function.

### C. Thermal conductivity

A large amount of experimental data is available in the literature, so that it is reasonable to focus the comparison with the theoretically computed values to the most reliable ones and to data extending to very high or low temperatures. Snel *et al.*,<sup>116</sup> Kestin *et al.*,<sup>117</sup> and Assael *et al.*<sup>118</sup> obtained zero-density thermal conductivity values from isothermal measurements as a function of density. All further data sets were corrected to the zero-density limit using the Rainwater-Friend theory<sup>91</sup> with the revised parameter ratios of Bich and Vogel,<sup>93</sup> since, in contrast to viscosity, the original parametrization of Rainwater and Friend yields poorer results for the initial density dependence of noble gas thermal conductivities (see Fig. 5.4 of Ref. 94).

In principle, the uncertainty of thermal conductivity measurements is inferior to that of viscosity. The standard uncertainty of the transient hot-wire (THW) technique, widely regarded to be the best experimental method, is estimated to be 0.2%–0.3% at room temperature, commonly increasing at lower and higher temperatures. This method was applied by Haarman,<sup>119</sup> Kestin *et al.*,<sup>117</sup> and Assael *et al.*,<sup>118</sup> but only Ref. 119 was concerned with measurements beyond room temperature. Using the hot-wire (HW) instrument under steady-state conditions or the concentric-cylinder (CC) method, the standard uncertainty worsens to about 1% near room temperature and to at least 2%–3% when the measurements are performed at other temperatures. Nesterov and Sudnik<sup>120</sup> employed the HW method at low temperatures down to 120 K, and Snel *et al.*<sup>116</sup> used it between 298 K and 348 K. Measurements by means of the CC technique were performed by Le Neindre and his co-workers<sup>121,122</sup> at room temperature and up to 608 K. The column method, which is a special variant of the CC method with a standard uncertainty of at least 3%, was applied by Faubert and Springer,<sup>123</sup> Jain and Saxena,<sup>124</sup> and Stefanov *et al.*<sup>125</sup> up to at most 2500 K. An uncertainty of 2% was reported by Hemminger<sup>126</sup> and by Hammerschmidt<sup>127</sup> for their measurements with a guarded parallel-plate (PP) apparatus. Furthermore, experimental data of Maštovský,<sup>128</sup> inferred from shock-tube (ST) measurements at very high temperatures up to 5000 K, are included in the comparison.

In Fig. 4, the selected experimentally based zero-density thermal conductivity data are compared with the theoretically calculated values. The THW data of Haarman<sup>119</sup> are characterized by small deviations of less than +0.2% up to 468 K, i.e., the temperature functions of the experimental data and of the theoretical values are perfectly consistent. The subsequent THW data of Kestin *et al.*<sup>117</sup> and Assael *et al.*<sup>118</sup> differ by +0.17% and +0.28%, respectively, while the CC results at room temperature of Tufeu *et al.*<sup>121</sup> and Le Neindre *et al.*<sup>122</sup> agree within  $\pm 0.5\%$ . The HW data of Snel *et al.*<sup>116</sup> disagree by less than +0.62% with the theoretical values, whereas the PP results of Hemminger<sup>126</sup> and of Hammerschmidt<sup>127</sup> show differences of  $-1.0\%$  to  $+0.25\%$  up

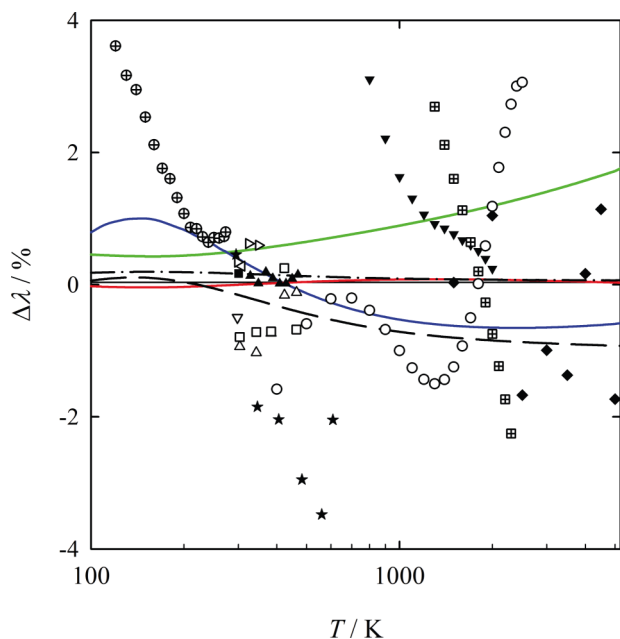


FIG. 4. Relative deviations of experimental and theoretical values for the thermal conductivity of krypton from those calculated using the pair potential  $V^{\text{tot}}$ . Experimental data: ★, Tufeu *et al.*;<sup>121</sup> ▼, Faubert and Springer;<sup>123</sup> ▲, Haarman;<sup>119</sup> ○, Jain and Saxena;<sup>124</sup> ⊕, Nesterov and Sudnik;<sup>120</sup> ⊞, Stefanov *et al.*;<sup>125</sup> ▷, Snel *et al.*;<sup>116</sup> ■, Kestin *et al.*;<sup>117</sup> ◁, Assael *et al.*;<sup>118</sup> ◆, Mašovský;<sup>128</sup> △, Hemminger;<sup>126</sup> ▽, Le Neindre *et al.*;<sup>122</sup> □, Hammer-schmidt.<sup>127</sup> Calculated values: (green line), potential of Aziz and Slaman;<sup>13</sup> (blue line), potential of Slavíček *et al.*;<sup>16</sup> (red line), potential of Waldrop *et al.*;<sup>19</sup> — —, this work using  $V^{\text{nonrel}}$ ; — · —, this work using  $V^{\text{DPT}2}$ ; uncertainty range is not shown for clarity.

to 463 K. The experimental data of Nesterov and Sudnik<sup>120</sup> at low temperatures are characterized by large positive deviations of up to +3.6%. The measurements up to moderately high temperatures of 600 K from Ref. 121 and those up to 2500 K from Refs. 123–125 show deviations of up to  $\pm 3.5\%$ , whereas the ST results of Mašovský<sup>128</sup> up to 5000 K agree with the computed values within  $\pm 1.7\%$ . In summary, the experimental data at low as well as at high temperatures do not enable to discriminate between different interatomic potential functions.

The relative differences between the thermal conductivity results for the pair potentials from the literature and those for the potential of the present work are almost identical to those obtained for viscosity, since both properties are directly linked for monatomic gases. Hence, no further discussion is necessary here.

#### D. Self-diffusion coefficient

In Fig. 5, we compare selected experimental self-diffusion data for dilute krypton gas, which were obtained from tracer-diffusion methods, and values computed for the Kr–Kr pair potentials from the literature with those resulting for the pair potential  $V^{\text{tot}}$  of the present work. A comprehensive compilation of the experimental data was provided by Winkelmann<sup>129</sup> and recently updated by Suárez-Iglesias *et al.*<sup>130</sup> Waldrop *et al.*<sup>19</sup> found deviations of up to  $\pm 9\%$  between the experimental data and their theoretical results. Hence, we only include the most accurate data with deviations

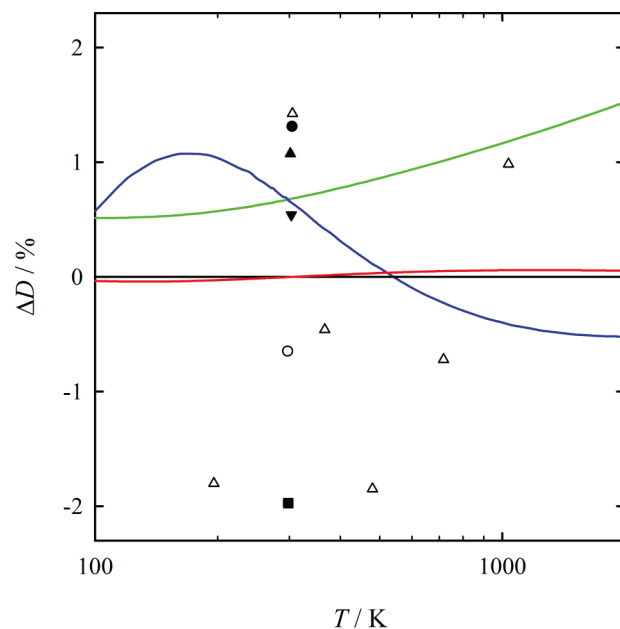


FIG. 5. Relative deviations  $\Delta D = [\rho_m D_{\text{self}} - \rho_m D_{\text{self}}(V^{\text{tot}})] / \rho_m D_{\text{self}}(V^{\text{tot}})$  of experimental and theoretical values for the self-diffusion coefficient of krypton from those calculated using the pair potential  $V^{\text{tot}}$ . Experimental data: ●, Srivastava and Paul;<sup>136</sup> ▲, Paul;<sup>132</sup> ▼, Saran and Singh;<sup>133</sup> △, Weissman and DuBro;<sup>134</sup> ■, Trappeniers and Michels;<sup>131</sup> ○, Benenson *et al.*<sup>135</sup> Calculated values: (green line), potential by Aziz and Slaman;<sup>13</sup> (blue line), potential by Slavíček *et al.*;<sup>16</sup> (red line), potential by Waldrop *et al.*;<sup>19</sup> uncertainty range is not shown for clarity.

within  $\pm 2\%$  in our comparison. Where necessary, the values of  $\rho_m D_{\text{self}}$  were calculated from the reported  $D_{\text{self}}$  data and the corresponding pressure assuming ideal gas behavior. No reliable theory for the initial density dependence of the self-diffusion coefficient is available in the literature. For this reason, and since Trappeniers and Michels<sup>131</sup> observed only a small difference between their extrapolated zero-density value of  $\rho_m D_{\text{self}}$  and the value at atmospheric pressure (about 0.05%), we did not correct the experimental data as was done for  $\eta$  and  $\lambda$ . Near room temperature, the data of Paul,<sup>132</sup> of Saran and Singh,<sup>133</sup> of Weissman and DuBro,<sup>134</sup> and of Benenson *et al.*<sup>135</sup> are in agreement with the theoretical values within the estimated experimental uncertainties of 1%–3%, whereas the deviations for the data of Srivastava and Paul<sup>136</sup> and of Trappeniers and Michels<sup>131</sup> exceed the uncertainties of the experimental data (1% and 0.7%, respectively). It is to be emphasized that the data of Weissman and DuBro agree with the theoretical values within  $\pm 2\%$  in the whole investigated temperature range from 196 to 1036 K. Note that this agreement is considerably better than reported by Waldrop *et al.*,<sup>19</sup> since they assigned all data tabulated in Ref. 134 to the work of Weissman and DuBro, although most of the data had been taken from older papers.

The values obtained for the *ab initio* pair potentials of Waldrop *et al.* and of the present work ( $V^{\text{tot}}$ ) differ by less than 0.06% for the complete temperature range, thus confirming that the theoretical results can be regarded as more reliable than any of the experimental data sets and also than the values obtained for the pair potentials of Aziz and Slaman<sup>13</sup> and of Slavíček *et al.*<sup>16</sup>



## VI. SUMMARY AND CONCLUSIONS

A comprehensive quantum-chemical study of the krypton-krypton interaction energy was carried out for 36 interatomic separations to develop a new potential energy curve for the krypton atom pair. In contrast to the recent pair potential of Waldrop *et al.*,<sup>19</sup> who used explicitly correlated coupled-cluster methods for the determination of the CBS limit of the interaction energy, we employed the standard orbital CCSD(T) approach in conjunction with very large basis sets, including a newly developed taV6Z basis set. The differences between the results for these two approaches were found to be significant. Our analysis of this inconsistency shows that CBS-extrapolated results for the interaction energy obtained from explicitly correlated CCSD(T) computations with basis sets limited to quintuple-zeta quality are not as accurate as those from orbital calculations with up to sextuple-zeta basis sets.

The impact of post-CCSD(T) electron correlation was accounted for by applying a stepwise scheme, where the full CCSDTQ method was used as the highest level of theory. This approach, along with larger basis sets compared to the ones utilized by Waldrop *et al.*, results in notable differences for the post-CCSD(T) correction. Furthermore, contributions to the interaction energy arising from core-core and core-valence correlation effects and from relativistic effects were investigated. The results for the core correction are in perfect agreement with those of Waldrop *et al.* For the relativistic correction, we found that the scalar relativistic calculations of the present work using the DPT2 method and those employed by Waldrop *et al.* using the DKH method give almost the same results. However, our four-component calculations including the Gaunt term revealed that contributions due to effects beyond the scalar relativistic level are not negligible.

The analytical potential function  $V^{\text{tot}}$ , which is based on the total interaction energies including all corrections, is characterized by a well depth of  $(200.88 \pm 0.51)$  K, whereas Waldrop *et al.* obtained a value of  $\varepsilon/k_B = (201.52 \pm 1.1)$  K. The values of  $\varepsilon/k_B$  for both *ab initio* potentials are in agreement with the value of 201.3 K for the empirical potential of Aziz and Slaman.<sup>13</sup> Regarding the  $C_6$  coefficients, the result for  $V^{\text{tot}}$  is in considerably closer agreement with the reference value from DOSD measurements<sup>58</sup> than the value of Waldrop *et al.*<sup>19</sup> This is partly due to the limited flexibility of the analytical function used in Ref. 19. However, even the  $C_6$  coefficient for the refitted version of the potential of Waldrop *et al.*, applying the more flexible analytical function of the present work, exhibits a deviation of  $-0.9\%$  from the DOSD value. Although this falls within the reported experimental uncertainty of 1%, the deviation is still distinctly larger than that for the potential of the present work (0.1%). Note that the theoretical  $C_6$  coefficients obtained for the state-of-the-art *ab initio* pair potentials of helium through argon<sup>3,6,9</sup> differ by no more than  $\pm 0.5\%$  from the corresponding DOSD values.

The computed vibrational dimer spectrum for  $V^{\text{tot}}$  is in agreement with that for the potential of Waldrop *et al.* and with the experimental data. Values for the second and third virial coefficients of krypton were calculated including quantum corrections for temperatures up to 5000 K. Unfortunately,

the scatter of the experimental data for the second virial coefficient of krypton is rather large, so that these data are of little use in assessing the quality of the *ab initio* pair potentials. Second virial coefficients based on highly accurate volumetric, acoustic, or dielectric measurements of gaseous krypton would facilitate a clear distinction between the pair potentials of Waldrop *et al.* and that of the present work. The EATM potential, which was adjusted to quantum-chemical nonadditive three-body interaction energies, shifts the third virial coefficient values of krypton only by a relatively small amount compared to the ATM potential. Therefore, both the ATM and EATM potentials can be regarded as valid approximations of the true nonadditive three-body potential of krypton.

The general framework for the computation of the dilute gas transport coefficients of pure monatomic substances is presented in terms of generalized cross sections in accordance with the classical transport theory of molecular gases. Values for the viscosity, the thermal conductivity, and the product of molar density and self-diffusion coefficient were computed for temperatures between 70 and 5000 K. Excellent agreement of the computed values for the viscosity with the most accurate experimental data was found at room temperature and especially with the data measured in our own group at temperatures up to 690 K. The discrepancies between the theoretical results and other experimental data can be largely resolved by rescaling the experimental data by means of viscosity ratios and theoretical reference values for argon. Unfortunately, the experimental viscosity data do not enable to definitely distinguish between the *ab initio* pair potential of Waldrop *et al.* and that of the present work, since the computed values for both potentials show surprisingly good agreement. We believe that this agreement is to some extent due to a cancellation of errors in the potential of Waldrop *et al.* Since measurements of thermal conductivity and self-diffusion are characterized by larger uncertainties than for viscosity, it is not possible to distinguish between the pair potentials using such data. On the contrary, the pair potentials can help to assess the quality of the experimental data sets for thermal conductivity and self-diffusion.

## ACKNOWLEDGMENTS

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