

# Ground state potential energy curves for He<sub>2</sub>, Ne<sub>2</sub>, Ar<sub>2</sub>, He-Ne, He-Ar, and Ne-Ar: A coupled-cluster study

Śławomir M. Cybulski, and Rafał R. Toczyłowski

Citation: *The Journal of Chemical Physics* **111**, 10520 (1999);

View online: <https://doi.org/10.1063/1.480430>

View Table of Contents: <http://aip.scitation.org/toc/jcp/111/23>

Published by the *American Institute of Physics*

---

## Articles you may be interested in

State-of-the-art correlated ab initio potential energy curves for heavy rare gas dimers: Ar<sub>2</sub>, Kr<sub>2</sub>, and Xe<sub>2</sub>

*The Journal of Chemical Physics* **119**, 2102 (2003); 10.1063/1.1582838

The van der Waals potentials between all the rare gas atoms from He to Rn

*The Journal of Chemical Physics* **118**, 4976 (2003); 10.1063/1.1543944

An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients

*The Journal of Chemical Physics* **80**, 3726 (1998); 10.1063/1.447150

Potential-Energy Curves for the He<sub>2</sub> Molecule

*The Journal of Chemical Physics* **52**, 4469 (2003); 10.1063/1.1673675

Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen

*The Journal of Chemical Physics* **90**, 1007 (1998); 10.1063/1.456153

A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu

*The Journal of Chemical Physics* **132**, 154104 (2010); 10.1063/1.3382344

---



# Ground state potential energy curves for He<sub>2</sub>, Ne<sub>2</sub>, Ar<sub>2</sub>, He–Ne, He–Ar, and Ne–Ar: A coupled-cluster study

Sławomir M. Cybulski and Rafał R. Toczyłowski

Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056

(Received 23 July 1999; accepted 20 September 1999)

Potential energy curves for three homonuclear (He<sub>2</sub>, Ne<sub>2</sub>, Ar<sub>2</sub>) and three heteronuclear (He–Ne, He–Ar, Ne–Ar) rare gas dimers are presented. The curves were calculated using several correlation consistent basis sets and the supermolecule single and double excitation coupled-cluster theory with noniterative perturbational treatment of triple excitations, CCSD(T). The most accurate results were obtained with the aug-cc-pV5Z basis set supplemented with an additional (3s3p2d2f1g) set of bond functions. The results obtained with a smaller aug-cc-pVQZ+(3s3p2d2f1g) basis set are almost as accurate. Both basis sets give results in better agreement with potentials based on experiments than the recent results obtained with larger *d*-aug-cc-pV6Z and *t*-aug-cc-pV6Z basis sets but without bond functions. For each complex and each basis set a fitted potential energy curve is given. In addition, for each complex, with the exception of He<sub>2</sub>, the values of  $R_e$ ,  $D_e$ ,  $B_0$ ,  $D_0$ , and  $\langle R \rangle_0$  are given. For He<sub>2</sub> no bound states were found so only the values of  $R_e$  and  $D_e$  are presented. For Ne<sub>2</sub>, Ar<sub>2</sub>, and Ne–Ar the calculated frequencies of vibrational and pure rotational transitions are shown to be in good agreement with the experimental results. © 1999 American Institute of Physics. [S0021-9606(99)30547-X]

## I. INTRODUCTION

It is convenient to divide *ab initio* calculations of interaction energies of two rare gas atoms into two groups. The first group comprises very accurate calculations for the helium dimer. The methods used in such calculations include a variational approach utilizing explicitly correlated Gaussian-type geminals,<sup>1,2</sup> explicitly correlated averaged coupled-pair functional,<sup>3</sup> multireference configuration interaction,<sup>4</sup> and quantum Monte-Carlo.<sup>5</sup> While the results obtained with various approaches are not yet in perfect agreement, they all seem to indicate that the well depth is approximately  $-11.0$  K ( $-34.8 \mu E_h$ ) at the interatomic separation of  $5.6 a_0$ . A somewhat stronger interaction ( $-11.06$  K) was found by Korona *et al.*<sup>6</sup> who developed their *ab initio* potential using symmetry-adapted perturbation theory (SAPT). A difference of less than  $0.1$  K ( $0.3 \mu E_h$ ) would be insignificant for virtually all other interactions but for He<sub>2</sub> it cannot be considered negligible. The SAPT potential has been called “the most accurate characterization of the helium interaction determined to date,”<sup>7</sup> but it has also been criticized as too attractive.<sup>4</sup> It is safe to assume that this controversy will lead to further studies.

The second group of *ab initio* calculations for rare gas dimers comprises all other calculations for all possible complexes excluding the just mentioned very accurate calculations for the helium dimer. The method of choice for the most recent calculations included in the second group is the supermolecule single and double excitation coupled-cluster theory with noniterative perturbational treatment of triple excitations CCSD(T).<sup>8</sup> Calculations of this type are usually performed with various conventional Gaussian-type basis sets although for He<sub>2</sub> Klopper and Noga<sup>9</sup> performed, among other things, CCSD(T) calculations using explicitly corre-

lated Gaussian-type functions. Their most accurate result for the well depth of the helium dimer is  $-10.68$  K ( $-33.82 \mu E_h$ ) and differs by approximately  $0.3$  K ( $1 \mu E_h$ ) from the accurate value given earlier. The results of only slightly inferior quality can also be obtained with conventional basis sets augmented with an additional set of bond functions as we will show in this work.

Calculations for other rare gas dimers are obviously not as accurate as those for the helium dimer, but because of the use of more sophisticated methods and the improving quality of basis sets they approach the accuracy of empirical potentials.<sup>10–12</sup> Unfortunately, the authors of the recent studies seemed more interested in the determination of the equilibrium interatomic distance,  $R_e$ , and the equilibrium dissociation energy,  $D_e$ , rather than the development of potential energy curves. Such curves would be of interest to, for example, researchers investigating larger clusters containing two or more rare gas atoms. Furthermore, in all recent CCSD(T) studies only homonuclear dimers He<sub>2</sub>, Ne<sub>2</sub>, and Ar<sub>2</sub> were considered. It is also of interest to investigate heteronuclear dimers for which extremely accurate rotational spectra became available in the last few years.<sup>13,14</sup> They can be used as a stringent test of *ab initio* calculations.

It is the purpose of this article to extend previous calculations and to develop the CCSD(T) potential energy curves for three homonuclear (He<sub>2</sub>, Ne<sub>2</sub>, Ar<sub>2</sub>) and three heteronuclear (He–Ne, He–Ar, Ne–Ar) complexes. By collecting all these systems in a single work we can better show the strengths and weaknesses of the state-of-the-art calculations of the interaction potentials for rare gas dimers. However, to keep the length of this work under control, it was necessary to make some compromises. For example, we compare our results with only the best available values. Fortunately, a

TABLE I. CCSD(T) interaction energies (in  $\mu E_h$ ) for  $\text{He}_2$  obtained with various basis sets.

R (Å)	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
1.750	5915.42	5775.88	5735.18	5779.70	5769.68	5736.36	5721.72
2.000	1818.44	1748.20	1725.64	1739.71	1734.72	1722.02	1716.26
2.250	494.82	463.11	450.11	452.48	449.81	445.40	443.24
2.500	96.65	83.14	76.13	74.75	73.16	71.73	71.00
2.750	-8.17	-14.00	-17.44	-19.46	-20.38	-20.87	-21.08
2.950	-25.97	-29.11	-30.99	-32.73	-33.34	-33.51	-33.58
2.975	-26.55	-29.47	-31.21	-32.90	-33.48	-33.63	-33.68
3.000	-26.91	-29.63	-31.24	-32.88	-33.44	-33.55	-33.61
3.025	-27.09	-29.62	-31.12	-32.70	-33.23	-33.33	-33.37
3.250	-23.92	-25.32	-26.10	-27.19	-27.54	-27.51	-27.53
3.500	-17.56	-18.34	-18.75	-19.38	-19.60	-19.55	-19.57
4.000	-8.44	-8.70	-8.83	-9.00	-9.10	-9.08	-9.09
5.000	-2.18	-2.21	-2.23	-2.25	-2.27	-2.26	-2.26

very thorough list of previous results obtained for homonuclear dimers has been compiled by van Mourik *et al.*<sup>12</sup> and we refer the interested reader to this recent work.

## II. METHODS

In 1994, Woon<sup>10</sup> convincingly showed that among several commonly available electron-correlated methods based on the single determinantal Hartree–Fock procedure the CCSD(T) approach gives the most reliable results for the homonuclear rare gas dimers. His work was the fifth in a series of “benchmark calculations with correlated molecular wave functions” which paved the way for a widespread acceptance of the correlation consistent basis sets developed by Dunning and co-workers.<sup>15–17</sup> In this work we use the augmented correlation consistent polarized triple, quadruple, and quintuple zeta basis sets. They are usually referred to as aug-cc-pVnZ ( $n=T, Q, 5$ ), but we will use the abbreviated notation avnZ employed in the MOLPRO package.<sup>18</sup> The main problem with the supermolecule calculations performed with conventional Gaussian-type basis sets for weakly interacting species is the difficulty of saturating the dispersion energy.<sup>19</sup> A very effective way of circumventing this problem is to use the bond functions (bf). For example, it has been shown<sup>20</sup> that a modest avtz basis set with an additional ( $3s3p2d$ ) set of bond functions recommended by Tao and Pan<sup>21</sup> gives the binding energy for the  $\text{HCl-Ar}$  complex which is in better agreement with the complete basis set (CBS) estimate than the result obtained with a much larger av5z basis set. The ( $3s3p2d$ ) set of Tao and Pan was developed for  $\text{He}_2$  and later used without any modifications for many other systems. Recently, several extended sets of bond functions were pro-

posed. For example, Koch *et al.*<sup>22</sup> extended Tao and Pan’s set by adding one  $f$ - and one  $g$ -symmetry function. Partridge and Bauschlicher<sup>23</sup> tested several sets of bond functions the largest of which was ( $6s6p6d3f3g3h$ ). We also tested a number of different sets of bond functions finally choosing a ( $3s3p2d2f1g$ ) set with the following exponents  $sp$ : 0.94, 0.34, 0.12;  $df$ : 0.64, 0.23;  $g$ : 0.35. To make the notation slightly more compact, the ( $3s3p2d$ ) set of Tao and Pan will be denoted as (332) and our ( $3s3p2d2f1g$ ) set as (33221). Overall, we report the results for seven basis sets; three without bond functions: avtz, avqz, and av5z, and four with bond functions: avtz+(332), avtz+(33221), avqz+(33221), and av5z+(33221).

We constructed the (33221) set by testing various modifications of Tao and Pan’s (332) set with the ratio of exponents in the set equal to 3.0 (as in the original set), 2.8, and 3.2, and with either more compact or more diffuse functions than in the original set. Test calculations on  $\text{Ne}_2$  and  $\text{Ar}_2$  revealed that the results obtained with the avtz+bf basis sets are very sensitive to the number and type of bond functions. Depending on the values of the exponents and their ratios these basis sets can either overestimate or underestimate the binding energy compared to the avqz+bf and av5z+bf results. Since in comparison with the av5z+(332) result the avtz+(332) basis set underestimates the CCSD(T) binding energy of  $\text{Ar}_2$  by approximately 3.5%, we wanted to construct a new set of bond functions that when used with the av5z basis set would lead to a stronger binding compared to av5z+(332), and when used with the avtz basis set would overestimate the binding energy compared to the av5z+bf value. We also wanted to keep the difference between avtz+bf, and av5z+bf results below 3.5%. By performing calculations for  $\text{Ar}_2$  with various avtz+bf, avqz+bf, and av5z+bf basis sets and monitoring the results we eventually found a (33221) set that satisfied our criteria. This strategy is time consuming, but it ensures that smaller basis sets do not give binding energies that significantly overestimate the CBS limit. An alternative approach that relies only on the optimization of binding energies with basis sets of triple zeta size can lead to erroneous results.

In all calculations the bond functions were located in the middle of the van der Waals bond. For each dimer and each basis set we performed calculations for at least thirteen different distances. In some cases we performed calculations for a few more distances but found that these additional points had only a very small impact on the equilibrium characteristics of the potential. For Ne and Ar only the valence electrons were correlated. The counterpoise procedure of Boys and Bernardi<sup>24</sup> was used to correct for basis set superposition

TABLE II. Characteristic properties of  $\text{He}_2$ . All seven *ab initio* potentials are too shallow to support a bound state.

Property	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Ref. value
$R_e (a_0)$	5.7552	5.6935	5.6564	5.6403	5.6317	5.6271	5.6245	5.6026 <sup>a</sup>
$D_e (\mu E_h)$	27.14	29.61	31.24	32.89	33.47	33.61	33.67	34.90 <sup>a</sup>

<sup>a</sup>Reference 7.

TABLE III. Parameters for the van der Waals potentials for He<sub>2</sub>.<sup>a</sup>

Parameter	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
$A$ ( $E_h$ )	5.905 23	6.461 97	6.075 00	6.471 93	6.594 54	6.641 33	6.620 02
$\alpha$ ( $a_0^{-1}$ )	1.818 58	1.866 31	1.829 26	1.869 37	1.881 60	1.887 08	1.885 53
$\beta$ ( $a_0^{-2}$ )	-0.075 1542	-0.070 0178	-0.075 6956	-0.066 6501	-0.064 0358	-0.063 5102	-0.063 9819
$b$ ( $a_0^{-1}$ )	1.595 25	1.662 57	1.693 57	1.819 78	1.864 00	1.863 21	1.858 22

$$^a C_6 = 1.460\,98\,E_h a_0^6; \quad C_8 = 14.1179\,E_h a_0^8; \quad C_{10} = 183.691\,E_h a_0^{10}; \quad C_{12} = 3.265\,27 \times 10^3\,E_h a_0^{12}; \quad C_{14} = 7.643\,99 \times 10^4\,E_h a_0^{14}; \quad C_{16} = 2.274\,72 \times 10^6\,E_h a_0^{16}.$$

error. All calculations were performed using MOLPRO 96.<sup>18</sup>

Unlike van Mourik *et al.*,<sup>12</sup> we focus exclusively on the CCSD(T) results and do not report the values obtained at lower levels of theory (SCF, MP2, CCSD), though they are available on request. The availability of efficient CCSD(T) programs<sup>25,26</sup> and computers with enough disk space and memory makes it easy to perform more accurate calculations than those reported here, but as stated earlier, one of the goals of this work is to develop parametrized potentials for interactions of rare gases that could be used to study larger clusters for which very large basis sets would be too expensive. An approach in which large basis sets are used to obtain two-body potentials and smaller ones to generate three-body potentials is inconsistent and because of that we chose basis sets which could be used for studying trimers and even larger clusters involving at least two rare gas atoms. The avtz+(332) and avtz+(33221) basis sets are the most likely candidates for such studies, though in the not too distant future it should become possible to use larger basis sets such as avqz+(33221). Because of its size the use of the av5z+(33221) basis set will, at least in the next few years, be probably limited to clusters of He.

To represent the interaction potentials of rare gas dimers, we use the same analytic representation that was used by Korona *et al.*<sup>6</sup> for the helium dimer. The potential includes a repulsive exponential component and an attractive truncated damped dispersion component and has the form

$$V(R) = A e^{-\alpha R + \beta R^2} + \sum_{n=3}^8 f_{2n}(R, b) \frac{C_{2n}}{R^{2n}}, \quad (1)$$

where  $A$ ,  $\alpha$ ,  $\beta$ , and  $b$  denote adjustable parameters,  $C_{2n}$  denotes a dispersion coefficient, and  $f_{2n}(R, b)$  denotes the damping function of Tang and Toennies<sup>27</sup>

$$f_{2n}(R, b) = 1 - e^{-bR} \sum_{k=0}^{2n} \frac{(bR)^k}{k!}. \quad (2)$$

We initially attempted to treat the three lowest dispersion coefficients,  $C_6$ ,  $C_8$ , and  $C_{10}$ , as adjustable parameters during the nonlinear least-square fitting procedure but in quite a few cases either  $C_8$  or  $C_{10}$  were found to be negative. Because of that we decided to use just one set of dispersion coefficients for a given system. For He<sub>2</sub> we use the most accurate  $C_6$ ,  $C_8$ , and  $C_{10}$  available.<sup>28</sup> For other systems we use the dispersion coefficients determined by fitting our *ab initio* results to the function given by Eq. (1) and choosing the set that gave the best agreement with the empirical estimates.<sup>29</sup> All subsequent fits were done with the values of

$C_6$ ,  $C_8$ , and  $C_{10}$  treated as constants. In all calculations the higher dispersion coefficients,  $C_{12}$ ,  $C_{14}$ , and  $C_{16}$ , were found from extrapolation formulas due to Thakkar.<sup>30</sup> Depending on the case, we used either Eq. (29) or Eq. (33) from Thakkar's work. From our tests and from a comparison with the results of van Mourik *et al.* for basis sets without bond functions we estimate that the inclusion of additional data during the fitting process or the use of different, but sufficiently flexible, forms of the potential should not affect the values of such properties as  $D_e$  and  $R_e$  by more than 0.3%.

Because our dispersion coefficients are only approximate, the fitting should be repeated when accurate CCSD(T) dispersion coefficients calculated with the correlation consistent basis sets become available. To facilitate this, we report not only the fitted parameters for each curve but also the original *ab initio* interaction energies. They may also be useful to those interested in testing new functional forms of the parametrized potential energy curves for rare gas dimers. As one of us<sup>31</sup> has shown in the past the nonexpanded dispersion interaction is not well represented by the truncated damped dispersion series used in Eq. (1). Furthermore, the series is in some cases divergent though this is not a major problem when it is truncated at the  $C_{16}$  term. Nonetheless, it would be preferable to use parametrized potentials free from such faults.

### III. RESULTS AND DISCUSSION

The results for each system are collected in three tables: the first table in each set contains the CCSD(T) results for 13

TABLE IV. CCSD(T) interaction energies (in  $\mu E_h$ ) for Ne<sub>2</sub> obtained with various basis sets.

R (Å)	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
2.250	3845.37	3635.34	3502.53	3561.42	3527.67	3469.48	3444.36
2.500	945.06	854.25	787.66	789.26	770.84	754.55	746.73
2.750	134.17	81.52	50.78	39.72	26.76	25.63	23.99
3.000	-57.02	-91.51	-107.72	-117.02	-125.56	-123.66	-123.67
3.075	-72.74	-102.80	-116.27	-124.81	-132.05	-130.23	-129.96
3.100	-75.93	-104.59	-117.34	-125.58	-132.33	-130.59	-130.44
3.125	-78.26	-105.50	-117.63	-125.67	-131.92	-130.27	-130.13
3.250	-81.28	-102.22	-111.79	-118.53	-122.75	-121.47	-121.23
3.500	-67.55	-79.24	-85.35	-90.25	-92.29	-91.02	-90.91
3.750	-49.58	-56.11	-59.92	-63.29	-64.98	-63.25	-63.24
4.000	-35.10	-38.87	-41.19	-43.29	-44.66	-43.17	-42.83
4.500	-17.36	-18.96	-19.84	-20.59	-20.83	-20.67	-20.61
5.000	-8.91	-9.78	-10.20	-10.46	-10.47	-10.54	-10.54



TABLE V. Characteristic properties of Ne<sub>2</sub>.

Property	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Ref. value
$R_e$ ( $a_0$ )	6.0755	5.9554	5.9055	5.8839	5.8585	5.8578	5.8559	5.841 <sup>a</sup>
$D_e$ ( $\mu E_h$ )	81.34	105.56	117.51	125.83	132.48	130.50	130.33	133.8 <sup>a</sup>
$\langle R \rangle_0$ ( $a_0$ )	6.7249	6.4941	6.4021	6.3565	6.3148	6.3194	6.3180	
$D_0$ ( $\mu E_h$ )	40.70	56.63	65.19	70.96	75.51	74.19	74.10	74.3 <sup>a</sup>
$B_0$ ( $\text{cm}^{-1}$ )	0.1377	0.1469	0.1509	0.1529	0.1548	0.1546	0.1547	0.17 <sup>b</sup>

<sup>a</sup>Reference 33.<sup>b</sup>Reference 42.

different distances obtained with the seven basis sets described earlier, the second one contains the characteristic properties of each potential energy curve, and the third one contains the fitted parameters for the analytical potentials. In general, we treat the results obtained with the av5z+(33221) basis set as the most reliable although in some cases the results obtained with the smaller avtz+(33221) and avqz+(33221) basis sets are in better agreement with experiment. After developing parametrized curves we used them to find the equilibrium interatomic separation,  $R_e$ , the equilibrium dissociation energy,  $D_e$ , the ground-vibrational-state dissociation energy,  $D_0$ , and rotational constant,  $B_0$ , as well as the average interatomic separation in the ground vibrational state,  $\langle R \rangle_0$ . The latter three quantities were found by solving the Schrödinger equation for nuclear motion using Le Roy's LEVEL program.<sup>32</sup> The tables contain only the results for the most common isotopes.

### A. Homonuclear Dimers

The results for He<sub>2</sub> are given in Tables I–III, for Ne<sub>2</sub> in Tables IV–VI, and for Ar<sub>2</sub> in Tables VII–IX. The agreement with the CCSD(T) results that van Mourik *et al.*<sup>12</sup> obtained with basis sets without bond functions is good with differences not exceeding 0.2%.

Even a very cursory analysis of the results in Tables II, V, and VIII shows that the use of basis sets augmented with bond functions improves agreement with either more accurate (He<sub>2</sub>)<sup>7</sup> or empirical results (Ne<sub>2</sub> and Ar<sub>2</sub>).<sup>33,34</sup> Even the smallest of the basis sets with bond functions, avtz+(332), gives the value of  $D_e$  that is in better agreement with the empirical result than the value of  $D_e$  obtained with much larger av5z basis set. Our two largest basis sets, avqz+(33221) and av5z+(33221), give results that agree better with the experimental data than the results obtained with a significantly larger *t*-aug-cc-pV6Z basis set (*d*-aug-cc-pV6Z for Ar<sub>2</sub>).

We note, however, that better agreement with experiment around the minimum does not necessarily guarantee that the same is true for the entire curve. For instance, at short distances the results obtained with the av5z basis are closer to the most accurate av5z+(33221) values than the results obtained with either avtz+(332) or avtz+(33221) basis sets. We also note that for Ne<sub>2</sub> and Ar<sub>2</sub> the results obtained with avtz+(33221) and avtz+(332) basis sets are significantly different. They lead to the well depths that are, respectively, deeper and shallower than those found with either avqz+(33221) or av5z+(33221) basis sets. The examination of the interaction energies at lower levels of theory reveals that these effects are caused primarily by the electron-correlated contribution to the interaction energy. For example, for Ar<sub>2</sub> at  $R=3.775$  Å the CCSD(T) interaction energies for the seven basis sets differ by as much as 144  $\mu E_h$ , whereas the SCF results are all within 5  $\mu E_h$ . At  $R=3.0$  Å, the CCSD(T) and SCF interaction energies for the seven basis sets differ by 763 and 48  $\mu E_h$ , respectively. Clearly, bond functions affect primarily the correlated portion of the interaction energy, but are unable to cure all the deficiencies of atom-centered basis sets. Even for a polarized triple zeta basis set the differences between results for different sets of bond functions can be significant. But it is also clear that the error committed by not using bond functions is far more serious. The results obtained with quadruple- and quintuple-zeta basis sets, as might be expected from their bigger size, are much less sensitive to the number and type of bond functions.

According to van Mourik *et al.*<sup>12</sup> the correlation consistent basis sets “have been shown to lead to systematic convergence to an apparent complete basis set (CBS) limit for a wide range of atomic properties, including dissociation energies, bond lengths, and vibrational frequencies.” Our results indicate that the extrapolation method used to obtain the

TABLE VI. Parameters for the van der Waals potential for Ne<sub>2</sub>.<sup>a</sup>

Parameter	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
$A$ ( $E_h$ )	33.8034	26.8956	70.1022	96.1335	80.2797	83.8788	88.5513
$\alpha$ ( $a_0^{-1}$ )	1.674 85	1.625 76	2.081 24	2.235 54	2.163 44	2.180 22	2.206 26
$\beta$ ( $a_0^{-2}$ )	−0.101 946	−0.100 425	−0.044 9408	−0.021 6719	−0.026 8459	−0.027 7265	−0.024 9851
$b$ ( $a_0^{-1}$ )	1.315 61	1.498 95	1.654 26	1.834 08	1.935 67	1.856 00	1.851 66

<sup>a</sup> $C_6=6.281\,74\,E_h a_0^6$ ;  $C_8=90.0503\,E_h a_0^8$ ;  $C_{10}=1679.45\,E_h a_0^{10}$ ;  $C_{12}=4.189\,67\times 10^4\,E_h a_0^{12}$ ;  $C_{14}=1.362\,98\times 10^6\,E_h a_0^{14}$ ;  $C_{16}=5.629\,06\times 10^7\,E_h a_0^{16}$ .

TABLE VII. CCSD(T) interaction energies (in  $\mu E_h$ ) for  $\text{Ar}_2$  obtained with various basis sets.

R (Å)	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
3.000	3818.45	3312.11	3156.12	3269.64	3175.30	3104.84	3054.98
3.250	949.78	680.99	587.03	617.70	557.65	538.68	518.11
3.500	-35.35	-172.64	-232.91	-233.33	-276.99	-271.11	-278.98
3.750	-300.99	-371.62	-410.57	-420.73	-451.80	-438.10	-440.82
3.775	-309.41	-375.72	-412.82	-423.36	-453.26	-439.53	-441.87
3.800	-315.76	-378.04	-413.57	-424.33	-453.03	-439.27	-441.32
3.850	-323.27	-378.32	-410.74	-421.86	-448.30	-434.64	-436.21
4.000	-316.67	-355.59	-380.09	-391.46	-411.42	-399.11	-399.60
4.250	-262.00	-285.52	-300.51	-310.28	-322.75	-313.34	-313.12
4.500	-199.89	-215.09	-224.33	-231.71	-239.45	-232.68	-232.30
5.000	-109.33	-115.93	-119.57	-123.15	-123.19	-123.19	-122.96
6.000	-35.05	-36.41	-37.05	-37.60	-37.81	-37.81	-37.77
7.000	-13.32	-13.72	-13.87	-13.85	-14.01	-13.97	-14.03

CBS values of  $R_e$  works well, but is not particularly reliable for  $D_e$ . It thus appears that the ability of the correlation consistent basis set to lead to the CBS limit “for a wide range” of properties should be reexamined. The use of sextuple-zeta basis sets certainly improved the reliability of extrapolation but serious problems remain. For example, the CBS value of  $D_e$  for  $\text{Ar}_2$  predicted by the  $d\text{-aug-cc-pVXZ}$  group of basis sets is in worse agreement with our most accurate results than the CBS value of  $D_e$  predicted by a smaller aug-cc-pVXZ group.

## B. Heteronuclear dimers

The results for He–Ne are given in Tables X–XII, for He–Ar in Tables XIII–XV, and for Ne–Ar in Tables XVI–XVIII. There were only several electron-correlated *ab initio* studies for these systems. In 1982, Clarke and Hinchliffe<sup>35</sup> reported the results of self consistent electron pair calculations for He–Ne and He–Ar. The quality of their results is poor by present standards, but better than the quality of the BSSE-uncorrected second-order Møller–Plesset perturbation theory (MP2) results reported by Ma *et al.*<sup>36</sup> in 1993. The MP4 results that Tao<sup>37</sup> obtained for He–Ne and He–Ar are much better and, for example, his equilibrium dissociation energies differ from our most accurate values by 5%–6%. The most recent work concerned with heteronuclear dimers appears to be a DFT study of Patton and Pederson.<sup>38</sup> The best results obtained with the Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA-PBE) functional are, unfortunately, very inaccurate and once again show the inability of the DFT approach to provide reliable results for

van der Waals interactions. The binding energies of He–Ne and He–Ar have errors of 139% and 52%, respectively, and the results for homonuclear dimers are of equally poor quality. In the light of these results it appears that only by fortunate accident the binding energy of Ne–Ar was found to be in excellent agreement with the empirical value.<sup>39</sup>

Our values of  $D_e$  and  $R_e$  for the three heteronuclear dimers are in good agreement with the values found using empirical potentials.<sup>40,41</sup> However, for He–Ne and He–Ar, the dissociation energies obtained with the av5z+(33221) basis set are larger than the empirical values. This strongly indicates that empirical potentials slightly underestimate the well depths for the two systems. This conclusion is based on a comparison of frequencies of vibrational and rotational transitions calculated using our *ab initio* potentials with the available spectroscopic data for  $\text{Ne}_2$ ,<sup>42</sup>  $\text{Ar}_2$ ,<sup>43,44</sup> and Ne–Ar.<sup>14</sup> It is clear that in each case our potentials are somewhat too shallow. It is also clear that our potentials for  $\text{He}_2$  are too shallow. Obviously, we expect that the *ab initio* potentials for He–Ne and He–Ar are too shallow as well.

## C. Vibrational energy levels

The most direct, but at the same time the most stringent test of calculated potential energy curves is to find the energy differences of rovibrational transitions and compare them with the experimental results. This section contains such an analysis for vibrational transitions for the three curves that support more than one bound vibrational levels. None of our potential energy curves for  $\text{He}_2$  is deep enough to support a bound vibrational state. This is not surprising since the well depth of our best curve is too shallow by slightly more than  $1 \mu E_h$  in comparison to more accurate curves<sup>6,7</sup> which support one bound level very close to the dissociation limit. For He–Ne we find only one bound vibrational level, in agreement with Ogilvie and Wang.<sup>39</sup> For He–Ar we also find only one bound level whereas Ogilvie and Wang found two states, with the higher one near the dissociation limit. The existence of the second level is difficult to reconcile with the fact that our best potentials are deeper than the one used by Ogilvie and Wang. It could simply be a result of their more approximate treatment of nuclear motion. But as we mentioned earlier the well depths of our best curves are underestimated so the existence of the first excited vibrational state for He–Ar should not be prematurely ruled out.

The remaining three dimers are more interesting as we find two bound states for  $\text{Ne}_2$ , eight for  $\text{Ar}_2$ , and four for Ne–Ar. In Table XIX we give the frequencies of vibrational transitions for each of our curves and compare them to either

TABLE VIII. Characteristic properties of  $\text{Ar}_2$ .

Property	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Ref. value
$R_e$ ( $a_0$ )	7.3559	7.2305	7.1773	7.1872	7.1504	7.1492	7.1403	7.107 <sup>a</sup>
$D_e$ ( $\mu E_h$ )	324.50	378.70	413.49	424.39	453.43	439.64	441.90	452.0 <sup>a</sup>
$\langle R \rangle_0$ ( $a_0$ )	7.5353	7.3939	7.3316	7.3384	7.2950	7.2975	7.2882	
$D_0$ ( $\mu E_h$ )	269.04	318.12	349.49	359.70	385.74	373.34	375.35	385.0 <sup>a</sup>
$B_0$ ( $\text{cm}^{-1}$ )	0.053 44	0.055 49	0.056 42	0.056 31	0.056 97	0.056 93	0.057 08	0.057 76 <sup>a</sup>

<sup>a</sup>Reference 44.

TABLE IX. Parameters for the van der Waals potential for Ar<sub>2</sub>.

Parameter	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
$A$ ( $E_h$ )	15.2998	55.4406	56.7325	111.130	88.3197	89.7045	82.9493
$\alpha$ ( $a_0^{-1}$ )	0.830 400	1.286 34	1.310 09	1.552 52	1.406 37	1.481 63	1.454 85
$\beta$ ( $a_0^{-2}$ )	-0.100 229	-0.060 1434	-0.055 2371	-0.025 5111	-0.037 2356	-0.034 5842	-0.037 9929
$b$ ( $a_0^{-1}$ )	1.240 91	1.356 99	1.454 15	1.769 11	2.095 42	1.660 99	1.623 65

$${}^a C_6 = 63.7520 E_h a_0^6; C_8 = 1556.46 E_h a_0^8; C_{10} = 4.94379 \times 10^4 E_h a_0^{10}; C_{12} = 2.072 89 \times 10^6 E_h a_0^{12}; C_{14} = 1.105 297 \times 10^8 E_h a_0^{14}; C_{16} = 7.247 72 \times 10^9 E_h a_0^{16}.$$

experimental or, if they are unavailable, to computational results obtained using empirical potentials. For Ar<sub>2</sub> we give the values for only three transitions. In general, the agreement between theory and experiment is directly proportional to the quality of the basis set. Basis sets with bond functions give results which are clearly superior to the ones obtained with basis sets containing only atom-centered functions. The results obtained with the avtz+(33221) basis set should be treated with some caution since it gives vibrational frequencies in good agreement with experiment only because of some fortunate imbalance in its makeup. The results obtained with larger avqz+(33221) and av5z+(33221) basis sets are more indicative of the accuracy of the state-of-the-art *ab initio* calculations for rare gas dimers. On the other hand, the values obtained with the avtz+(33221) basis set are helpful in establishing the well depths that are consistent with the experimental results.

The frequency of the  $v'=3 \leftarrow v''=2$  transition for Ne–Ar obtained from an empirical potential by Ogilvie and Wang<sup>39</sup> is inconsistent with the trend that we observe for frequencies based on *ab initio* calculations. The correct value should be equal to approximately  $3.85 \text{ cm}^{-1}$ .

#### D. Rotational energy levels

In Table XX we give the energy differences between low rotational states of the ground vibrational state for all dimers except He<sub>2</sub>. For heteronuclear dimers it is possible to compare them directly with pure rotational microwave transitions. For He–Ne and He–Ar such transitions remain to be measured, but for Ne–Ar Grabow *et al.*<sup>14</sup> reported the frequencies of three transitions: 1–0, 2–1, 3–2. Because of the high sensitivity and resolution of the Fourier-transform microwave spectrometer their results are extremely accurate. Our best results are within 0.8% of the experimental values but that is approximately 100 000 times worse than the experimental accuracy. From the examination of basis set trends we conclude that for He–Ne our best results are more accurate than the values calculated using empirical potentials.<sup>39</sup> For He–Ar our results and those of Ogilvie and Wang are very similar. In all likelihood they underestimate the actual frequencies of rotational transitions.

For homonuclear dimers the energies of rotational levels can be found from observed rovibronic bands.<sup>43,44</sup> For Ar<sub>2</sub> Colbourn and Douglas<sup>43</sup> were the first to report the appropriate rotational constants, but the most accurate values available today are those of Herman *et al.*<sup>44</sup> Our best calculated values underestimate the experimental frequencies by

slightly more than 1%. For Ne<sub>2</sub> accurate rotational constants are not available and we can only estimate that our most accurate results are in error by approximately 1%.

#### IV. SUMMARY

We have presented results of *ab initio* calculations for six rare gas dimers. For each dimer we have presented the actual CCSD(T) interaction energies as well as parametrized potential energy curves and some characteristic properties. By supplementing the atom-centered basis sets with bond functions we have obtained results that for some properties are within 1% of the experimental values. For He–Ne and He–Ar our best potential energy curves are probably more reliable than the best available empirical curves. For Ne<sub>2</sub> and Ne–Ar our curves are not as accurate as their empirical counterparts, but are more accurate than all previous *ab initio* curves. In the case of Ar<sub>2</sub> neither our av5z+33221 nor a slightly better *d*-aug-cc-pV5Z-33211 potential developed recently by Fernández and Koch<sup>45</sup> are as accurate as the empirical curve.<sup>34</sup> We intend to use the avtz+(33221) and avqz+(33221) basis sets to study larger weakly interacting clusters and the present results give us confidence that they will provide accurate results.

One of the limitations of this work is that in calculations for Ne and Ar only the valence electrons were correlated. As van Mourik *et al.*<sup>12</sup> showed for Ne<sub>2</sub> and Ar<sub>2</sub> the core–core and core–valence contributions to the interaction energies

TABLE X. CCSD(T) interaction energies (in  $\mu E_h$ ) for He–Ne obtained with various basis sets.

R (Å)	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
2.000	4601.24	4420.02	4342.03	4401.27	4379.82	4334.84	4315.20
2.250	1301.03	1220.26	1177.09	1192.16	1180.67	1164.38	1157.77
2.500	294.34	255.63	233.70	232.87	225.98	221.57	219.25
2.750	16.47	-3.68	-14.69	-19.19	-22.92	-23.83	-24.48
3.000	-43.36	-54.46	-60.21	-64.09	-66.09	-66.19	-66.30
3.025	-44.85	-55.36	-60.68	-64.49	-66.42	-66.50	-66.55
3.050	-45.91	-55.85	-60.85	-64.52	-66.36	-66.40	-66.43
3.250	-44.68	-51.03	-54.16	-56.72	-58.19	-57.88	-57.88
3.500	-34.36	-37.99	-39.83	-41.39	-42.58	-42.02	-42.01
3.750	-24.42	-26.54	-27.63	-28.62	-29.41	-28.93	-28.93
4.000	-17.02	-18.29	-18.93	-19.59	-20.01	-19.73	-19.47
4.500	-8.40	-8.93	-9.16	-9.44	-9.54	-9.49	-9.43
5.000	-4.39	-4.65	-4.73	-4.83	-4.86	-4.87	-4.87

TABLE XI. Characteristic properties of He–Ne.

Property	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Ref. value
$R_e (a_0)$	5.9076	5.8137	5.7643	5.7455	5.7283	5.7251	5.7224	5.7362 <sup>a</sup>
$D_e (\mu E_h)$	46.99	55.85	60.80	64.52	66.52	66.42	66.57	66.15 <sup>a</sup>
$\langle R \rangle_0 (a_0)$	8.4416	7.9397	7.7221	7.5970	7.5296	7.5263	7.5195	
$D_0 (\mu E_h)$	5.80	8.33	9.86	11.01	11.64	11.65	11.71	
$B_0 (\text{cm}^{-1})$	0.2995	0.3298	0.3449	0.3538	0.3590	0.3594	0.3599	

<sup>a</sup>Reference 40.

TABLE XII. Parameters for the van der Waals potentials for He–Ne.

Parameter	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
$A (E_h)$	14.2411	16.8870	20.0657	21.1723	24.0016	26.0488	24.4219
$\alpha (a_0^{-1})$	1.801 55	1.908 07	1.998 11	2.031 94	2.030 03	2.065 04	2.057 66
$\beta (a_0^{-2})$	−0.079 5265	−0.063 1155	−0.050 2687	−0.038 9772	−0.036 0216	−0.032 0947	−0.032 3443
$b (a_0^{-1})$	1.469 97	1.649 32	1.780 25	2.081 64	2.745 01	2.789 16	2.656 28

<sup>a</sup> $C_6=3.052\ 39\ E_h a_0^6$ ;  $C_8=31.6787\ E_h a_0^8$ ;  $C_{10}=427.732\ E_h a_0^{10}$ ;  $C_{12}=7725.16\ E_h a_0^{12}$ ;  $C_{14}=1.819\ 45 \times 10^5\ E_h a_0^{14}$ ;  $C_{16}=5.440\ 12 \times 10^6\ E_h a_0^{16}$ .

TABLE XIII. CCSD(T) interaction energies (in  $\mu E_h$ ) for He–Ar obtained with various basis sets.

R (Å)	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
2.250	8598.49	8236.53	8120.01	8273.23	8219.37	8122.88	8076.01
2.500	2981.14	2786.02	2723.46	2783.35	2756.20	2712.44	2692.53
2.750	914.96	816.12	780.95	799.71	785.79	766.68	758.45
3.000	201.26	153.24	133.05	135.54	127.31	120.24	117.06
3.250	−18.54	−41.85	−53.52	−56.18	−61.35	−63.02	−64.24
3.475	−67.11	−79.84	−86.82	−90.29	−93.71	−93.56	−94.04
3.500	−68.70	−80.64	−87.25	−90.69	−93.97	−93.72	−94.13
3.525	−69.83	−81.04	−87.27	−90.70	−93.83	−93.48	−93.85
3.750	−66.83	−73.40	−77.16	−79.99	−82.10	−81.35	−81.45
4.000	−52.98	−56.82	−58.98	−61.00	−62.37	−61.65	−61.67
4.500	−28.60	−30.01	−30.77	−31.67	−32.26	−31.83	−31.77
5.000	−15.21	−15.77	−16.05	−16.45	−16.69	−16.49	−16.48
6.000	−4.91	−4.91	−5.10	−5.16	−5.20	−5.17	−5.18

TABLE XIV. Characteristic properties of He–Ar.

Property	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Ref. value
$R_e (a_0)$	6.7970	6.6908	6.6411	6.6364	6.6181	6.6056	6.5998	6.5718 <sup>a</sup>
$D_e (\mu E_h)$	71.01	80.98	87.26	90.72	94.01	93.73	94.15	93.89 <sup>a</sup>
$\langle R \rangle_0 (a_0)$	8.1690	7.9301	7.8111	7.7679	7.7165	7.7107	7.7014	
$D_0 (\mu E_h)$	20.80	25.52	28.54	30.24	31.94	31.75	31.96	
$B_0 (\text{cm}^{-1})$	0.2663	0.2808	0.2884	0.2911	0.2945	0.2950	0.2957	

<sup>a</sup>Reference 40.TABLE XV. Parameters for the van der Waals potentials for He–Ar.<sup>a</sup>

Parameter	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
$A (E_h)$	18.8774	21.8171	21.9118	23.7566	26.3607	23.3061	23.1693
$\alpha (a_0^{-1})$	1.535 45	1.596 07	1.601 91	1.643 13	1.694 22	1.635 15	1.633 29
$\beta (a_0^{-2})$	−0.059 0724	−0.053 8631	−0.052 3797	−0.044 2523	−0.035 7070	−0.045 7403	−0.046 2008
$b (a_0^{-1})$	1.364 30	1.443 05	1.510 99	1.631 72	1.769 88	1.641 66	1.63719

<sup>a</sup> $C_6=9.387\ 01\ E_h a_0^6$ ;  $C_8=165.522\ E_h a_0^8$ ;  $C_{10}=3797.16\ E_h a_0^{10}$ ;  $C_{12}=1.165\ 18 \times 10^5\ E_h a_0^{12}$ ;  $C_{14}=4.662\ 58 \times 10^6\ E_h a_0^{14}$ ;  $C_{16}=2.368\ 61 \times 10^8\ E_h a_0^{16}$ .



TABLE XVI. CCSD(T) interaction energies (in  $\mu E_h$ ) for Ne–Ar obtained with various basis sets.

R ( $\text{\AA}$ )	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
2.500	6978.94	6559.88	6368.37	6528.01	6434.88	6332.11	6278.42
2.750	2138.74	1918.36	1817.03	1864.46	1813.48	1774.84	1754.13
3.000	492.18	372.42	317.71	322.16	293.37	282.27	275.00
3.250	-12.12	-79.52	-110.46	-117.59	-135.07	-136.02	-138.26
3.475	-126.26	-167.84	-187.57	-195.29	-206.66	-204.95	-205.62
3.500	-130.50	-169.84	-188.69	-196.33	-207.11	-205.29	-205.83
3.525	-133.60	-170.94	-188.82	-196.35	-206.68	-204.66	-205.28
3.750	-131.69	-155.30	-166.91	-173.55	-180.01	-177.52	-177.61
4.000	-105.41	-119.74	-126.99	-132.49	-136.39	-133.82	-133.58
4.250	-78.56	-87.29	-91.81	-96.02	-98.25	-96.21	-96.06
4.500	-57.08	-62.57	-65.48	-68.45	-69.48	-68.32	-67.90
5.000	-30.23	-32.55	-33.80	-34.96	-35.29	-34.90	-34.91
6.000	-9.61	-10.29	-10.53	-10.40	-10.63	-10.75	-10.78

TABLE XVII. Characteristic properties of Ne–Ar.

Property	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Ref. value
$R_e$ ( $a_0$ )	6.8378	6.7040	6.6489	6.6425	6.6139	6.6067	6.6015	6.5453 <sup>a</sup>
$D_e$ ( $\mu E_h$ )	137.64	170.95	188.65	196.78	207.40	205.32	205.87	208.62
$\langle R \rangle_0$ ( $a_0$ )	7.2131	7.0294	6.9533	6.9378	6.8990	6.8945	6.8889	
$D_0$ ( $\mu E_h$ )	93.12	119.54	133.97	140.53	149.26	147.48	147.95	149.86 <sup>a</sup>
$B_0$ ( $\text{cm}^{-1}$ )	0.088 28	0.092 78	0.094 76	0.095 14	0.096 18	0.096 32	0.096 47	0.097 23 <sup>a</sup>

<sup>a</sup>Reference 14.TABLE XVIII. Parameters for the van der Waals potentials for Ne–Ar.<sup>a</sup>

Parameter	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)
$A$ ( $E_h$ )	35.8348	46.6754	65.6124	72.4929	86.4187	75.5400	75.4390
$\alpha$ ( $a_0^{-1}$ )	1.403 66	1.526 90	1.681 81	1.728 05	1.811 68	1.749 06	1.749 39
$\beta$ ( $a_0^{-2}$ )	-0.079 7404	-0.065 5512	-0.047 0223	-0.038 7822	-0.026 1448	-0.036 4691	-0.036 7715
$b$ ( $a_0^{-1}$ )	1.253 23	1.393 96	1.502 99	1.603 98	1.751 80	1.637 77	1.630 79

<sup>a</sup> $C_6=19.0098 E_h a_0^6$ ;  $C_8=392.861 E_h a_0^8$ ;  $C_{10}=1.05627 \times 10^4 E_h a_0^{10}$ ;  $C_{12}=3.798 79 \times 10^5 E_h a_0^{12}$ ;  $C_{14}=1.781 60 \times 10^7 E_h a_0^{14}$ ;  $C_{16}=1.060 75 \times 10^9 E_h a_0^{16}$ .TABLE XIX. Energy differences (in  $\text{cm}^{-1}$ ) between vibrational levels of an indicated dimer.

Dimer	$v' - v''$	avtz	avqz	av5z	avtz+ (332)	avtz+ (33221)	avqz+ (33221)	av5z+ (33221)	Empirical
Ne <sub>2</sub>	1-0	8.01	10.71	12.07	12.98	13.69	13.47	13.46	13.70 <sup>a</sup>
Ar <sub>2</sub>	1-0	20.40	22.66	24.14	24.52	25.79	25.17	25.27	25.69 <sup>b</sup>
Ar <sub>2</sub>	2-1	15.38	17.60	19.00	19.44	20.61	20.03	20.11	20.58 <sup>b</sup>
Ar <sub>2</sub>	3-2	10.81	12.85	14.11	14.57	15.59	15.08	15.15	15.58 <sup>b</sup>
Ne–Ar	1-0	13.00	15.74	17.13	17.78	18.58	18.42	18.45	18.79 <sup>c</sup>
Ne–Ar	2-1	5.94	7.90	8.98	9.47	10.12	9.98	10.01	10.27 <sup>d</sup>
Ne–Ar	3-2	1.47	2.44	3.02	3.27	3.64	3.57	3.60	2.44 <sup>d</sup>

<sup>a</sup>Experimental result of Tanaka and Yoshino (Ref. 42).<sup>b</sup>Experimental result of Herman *et al.* (Ref. 44).<sup>c</sup>Experimental result of Grabow *et al.* (Ref. 14).<sup>d</sup>Calculated by Ogilvie and Wang (Ref. 39) using an empirical potential.

TABLE XX. Energy differences (in  $\text{cm}^{-1}$ ) between rotational levels of the ground vibrational state of an indicated dimer.

Dimer	$J' - J''$	avtz	avqz	av5z (332)	avtz+ (33221)	avtz+ (33221)	avqz+ (33221)	av5z+	Empirical
Ne <sub>2</sub>	1-0	0.2752	0.2936	0.3016	0.3055	0.3094	0.3091	0.3092	0.34 <sup>a</sup>
Ne <sub>2</sub>	2-1	0.5486	0.5859	0.6020	0.6101	0.6178	0.6171	0.6174	...
Ne <sub>2</sub>	3-2	0.8183	0.8755	0.9000	0.9124	0.9240	0.9229	0.9233	...
Ne <sub>2</sub>	4-3	1.0823	1.1608	1.1942	1.2112	1.2270	1.2253	1.2259	...
Ar <sub>2</sub>	1-0	0.1069	0.1109	0.1128	0.1126	0.1139	0.1139	0.1142	0.1155 <sup>b</sup>
Ar <sub>2</sub>	2-1	0.2138	0.2219	0.2257	0.2252	0.2279	0.2277	0.2283	0.2310 <sup>b</sup>
Ar <sub>2</sub>	3-2	0.3205	0.3329	0.3384	0.3378	0.3417	0.3415	0.3423	0.3464 <sup>b</sup>
Ar <sub>2</sub>	4-3	0.4272	0.4435	0.4511	0.4502	0.4556	0.4553	0.4565	0.4618 <sup>b</sup>
He-Ne	1-0	0.5806	0.6457	0.6775	0.6965	0.7074	0.7081	0.7092	0.7060 <sup>c</sup>
He-Ne	2-1	0.9941	1.1715	1.2583	1.3083	1.3349	1.3361	1.3387	1.3480 <sup>c</sup>
He-Ar	1-0	0.5300	0.5594	0.5748	0.5802	0.5871	0.5881	0.5895	0.5897 <sup>c</sup>
He-Ar	2-1	1.0433	1.1043	1.1365	1.1480	1.1624	1.1644	1.1671	1.1670 <sup>c</sup>
He-Ar	3-2	1.5161	1.6159	1.6682	1.6880	1.7114	1.7138	1.7180	1.7170 <sup>c</sup>
He-Ar	4-3	1.8868	2.0564	2.1394	2.5145	2.2094	2.2112	2.2172	...
Ne-Ar	1-0	0.1765	0.1855	0.1895	0.1903	0.1923	0.1926	0.1929	0.1944 <sup>d</sup>
Ne-Ar	2-1	0.3528	0.3709	0.3788	0.3803	0.3845	0.3850	0.3856	0.3887 <sup>d</sup>
Ne-Ar	3-2	0.5285	0.5557	0.5676	0.5700	0.5763	0.5771	0.5780	0.5826 <sup>d</sup>
Ne-Ar	4-3	0.7034	0.7399	0.7559	0.7591	0.7675	0.7685	0.7698	0.7759 <sup>d</sup>

<sup>a</sup>Based on  $B_0$  given by Tanaka and Yoshino (Ref. 42).<sup>b</sup>Based on  $B_0$  and  $D_0$  given by Herman *et al.* (Ref. 44).<sup>c</sup>Calculated by Ogilvie and Wang (Ref. 39) using an empirical potential.<sup>d</sup>Based on  $B_0$ ,  $D_0$ , and  $H_0$  given by Grabow *et al.* (Ref. 14).

are small but not negligible. Future calculations should certainly examine these contributions using appropriate basis sets with bond functions.

## ACKNOWLEDGMENT

We acknowledge the support of National Science Foundation (Grant No. CHE-9616683).

<sup>1</sup>J. Komasa and J. Rychlewski, *Mol. Phys.* **91**, 909 (1997).<sup>2</sup>J. Komasa, *J. Chem. Phys.* **110**, 7909 (1999).<sup>3</sup>R. J. Gdanitz, *Mol. Phys.* **96**, 1423 (1999).<sup>4</sup>J. van de Bovenkamp and F. B. van Duijneveldt, *J. Chem. Phys.* **110**, 11141 (1999).<sup>5</sup>J. B. Anderson, C. A. Traynor, and B. M. Boghosian, *J. Chem. Phys.* **99**, 345 (1993).<sup>6</sup>T. Korona, H. L. Williams, R. Bukowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **106**, 5109 (1997).<sup>7</sup>A. R. Janzen and R. A. Aziz, *J. Chem. Phys.* **107**, 914 (1997).<sup>8</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).<sup>9</sup>W. Klopper and J. Noga, *J. Chem. Phys.* **103**, 6127 (1995).<sup>10</sup>D. E. Woon, *J. Chem. Phys.* **100**, 2838 (1994).<sup>11</sup>J. V. Burda, R. Zahradnik, P. Hobza, and M. Urban, *Mol. Phys.* **89**, 425 (1996).<sup>12</sup>T. van Mourik, A. K. Wilson, and T. H. Dunning, Jr., *Mol. Phys.* **96**, 529 (1999).<sup>13</sup>W. Jäger, Y. Xu, and M. C. L. Gerry, *J. Chem. Phys.* **99**, 919 (1993).<sup>14</sup>J.-U. Grabow, A. S. Pine, G. T. Fraser, F. J. Lovas, R. D. Suenram, T. Emilsson, E. Arunan, and H. S. Gutowsky, *J. Chem. Phys.* **102**, 1181 (1995).<sup>15</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).<sup>16</sup>R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).<sup>17</sup>D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).<sup>18</sup>MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P.

J. Knowles with contributions from J. Almlöf, R. D. Amos, A. Berning, M. J. O. Deegan, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schuetz, H. Stoll, T. Thorsteinsson, and D. L. Cooper.

<sup>19</sup>M. Gutowski, J. Verbeek, J. H. van Lenthe, and G. Chałasiński, *Chem. Phys.* **111**, 271 (1987).<sup>20</sup>S. M. Cybulski and J. S. Holt, *J. Chem. Phys.* **110**, 7745 (1999).<sup>21</sup>F.-M. Tao and Y.-K. Pan, *J. Chem. Phys.* **97**, 4989 (1992).<sup>22</sup>H. Koch, B. Fernandez, and O. Christiansen, *J. Chem. Phys.* **108**, 2784 (1998).<sup>23</sup>H. Partridge and C. W. Bauschlicher, Jr., *Mol. Phys.* **96**, 705 (1999).<sup>24</sup>S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).<sup>25</sup>C. Hampel, K. A. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992).<sup>26</sup>M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.* **227**, 321 (1994).<sup>27</sup>K. T. Tang and J. P. Toennies, *J. Chem. Phys.* **80**, 3726 (1984).<sup>28</sup>D. M. Bishop and J. Pipin, *Int. J. Quantum Chem.* **45**, 349 (1993).<sup>29</sup>K. T. Tang and J. P. Toennies, *Z. Phys. D: At., Mol. Clusters* **1**, 91 (1986).<sup>30</sup>J. Thakkar, *J. Chem. Phys.* **89**, 2092 (1988).<sup>31</sup>S. M. Cybulski, *J. Chem. Phys.* **96**, 8225 (1992).<sup>32</sup>R. J. Le Roy, Chemical Physics Research Report CP-555R, University of Waterloo (1996).<sup>33</sup>R. A. Aziz and M. J. Slaman, *Chem. Phys.* **130**, 187 (1989).<sup>34</sup>R. A. Aziz, *J. Chem. Phys.* **99**, 4518 (1993).<sup>35</sup>J. H. R. Clarke and A. Hinchliffe, *Adv. Mol. Relax. Processes* **22**, 133 (1982).<sup>36</sup>N. L. Ma, W.-K. Li, and C. Y. Ng, *J. Chem. Phys.* **99**, 3617 (1993).<sup>37</sup>F.-M. Tao, *J. Chem. Phys.* **98**, 3049 (1993).<sup>38</sup>D. C. Patton and M. R. Pederson, *Int. J. Quantum Chem.* **69**, 619 (1998).<sup>39</sup>J. F. Ogilvie and F. Y. H. Wang, *J. Mol. Struct.* **291**, 313 (1993).<sup>40</sup>M. Keil, L. J. Danielson, and P. J. Dunlop, *J. Chem. Phys.* **94**, 296 (1991).<sup>41</sup>D. A. Barrow and R. A. Aziz, *J. Chem. Phys.* **89**, 6189 (1988).<sup>42</sup>Y. Tanaka and K. Yoshino, *J. Chem. Phys.* **57**, 2964 (1972).<sup>43</sup>E. A. Colbourn and A. E. Douglas, *J. Chem. Phys.* **65**, 1741 (1976).<sup>44</sup>P. R. Herman, P. E. LaRocque, and B. P. Stoicheff, *J. Chem. Phys.* **89**, 4535 (1988).<sup>45</sup>B. Fernández and H. Koch, *J. Chem. Phys.* **109**, 10255 (1998).