New basis sets for the evaluation of interaction energies: an *ab initio* study of the He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar and Ne–Ar van der Waals complex internuclear potentials and ro-vibrational spectra†

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We investigated the performance of medium-size basis sets in calculations of interaction energies for small van der Waals complexes. After careful numerical tests we derived new efficient basis sets (modified LPol-*n* bases, MLPol-*n*) for the evaluation of the interaction energies for He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar and Ne–Ar complexes. Additionally, we carried out systematic basis set studies taking as a starting point Jensen's aug-pc-2 basis set. In both cases we considered the addition of midbond functions to the bases. The proposed MLPol-*n* sets use the model of a harmonic oscillator embedded in an external electric field and belong to the family of Pol bases. The quality of the MLPol-*n* sets was first tested through finite-field Hartree–Fock atomic polarizability calculations. Next we obtained coupled cluster singles and doubles (CCSD), including connected triples, CCSD(T), interaction potentials for the six van der Waals complexes, and taking as reference the most accurate theoretical values available in the literature, we implemented new basis sets for the evaluation of the interaction energies. To test the potentials further we used them to calculate the ro-vibrational spectra for the complexes. The results are in very good agreement with the experimental data. In the future, we plan to extend the study to larger van der Waals complexes.

I Introduction

Van der Waals complexes are characterized by the presence of weak bonds between nonpolar systems. The intermolecular interactions are therefore dominated by dispersion forces. These clusters are used as important targets for studying the dispersion interaction, which plays an important role in processes like the solvation or adsorption of molecules.[1,2] From the theoretical point of view the dispersion interaction is the most demanding. Not only large basis sets, but also accurate electron correlation methods are required to give an adequate description of the dispersion. State-of-the-art *ab initio* results can compete with the best available experimental data often obtained using highly sophisticated experimental settings. But these calculations require a large computational effort, and they get prohibitive in the case of large molecular complexes (more than 10 heavy atoms).

To evaluate the ro-vibrational spectra of van der Waals complexes, accurate Intermolecular Potential Energy Surfaces (IPESs) are mandatory. Among the computational methods tested, the coupled cluster singles and doubles including connected triples corrections (CCSD(T))[3] method has been shown to yield highly accurate interaction energies if combined with sufficiently large and diffuse basis sets, *i.e.* of aug-cc-pVDZ[4] or higher quality basis sets with extra midbond functions.[5] The size of the basis set used in a computational study is, however, limited by the size of the system under investigation. Especially in the case of methods as computationally expensive as CCSD(T), which scales as N^7 with N being the number of basis functions, the size of the basis set needs to be kept as small as possible in order to avoid a substantial increase in the computing time, but not so small that the results are significantly less accurate.

In order to investigate a possible reduction in computing effort for calculations of van der Waals complex interaction energies, one solution is to reduce the CCSD(T) scaling. We tackled this when implementing the CCSD(T) code using the Cholesky decomposition in the orbital energy denominators.[6] Another solution is to develop new medium-size basis sets, adequate and accurate enough for studying van der Waals complexes. In the present study we consider the latter solution and develop medium-size basis sets for He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar and Ne–Ar van der Waals complexes. After selecting the most accurate medium-size bases, we obtain the corresponding Intermolecular Potentials and test them by using them to calculate the ro-vibrational spectra for the complexes. Both here and in the basis set development, we consider as a reference the most accurate theoretical results available in the literature.

The new sets, abbreviated as 'MLPol' (modified large polarized basis sets), belong to the family of Pol sets designed by Sadlej and co-workers over the decades.[7–15] Additionally,

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we use the augmented polarization-consistent aug-pc-2 basis set by Jensen (abbreviated as 'apc2' throughout).[16] This set yielded promising results in our latest work on hydrogen-bonded complexes,[17] where the quality of the apc2 results was comparable with that of those obtained using larger Dunning's basis sets. In both cases we consider the addition of midbond functions to the bases.

MLPol sets were generated for He, Ne and Ar using the procedure described in ref. 15 and only briefly recapitulated here. The close resemblance of the solutions of the harmonic oscillator Schrödinger equation to the Gaussian-type orbitals (GTOs) used commonly in *ab initio* and DFT calculations led to the idea of extending some source sets of functions with polarization functions resulting from the model of a harmonic oscillator perturbed by an external electric field. Originally, the external perturbation was considered to be static and this led to time-independent solutions.[7,8,10] In the last decade the investigation was generalized to the case of time-dependent fields[11] and resulted in the generation of two new types of polarized sets, the reduced-size ZPol sets,[12–14] designed for calculating the linear electric properties of large molecules, and the large LPol-*n* (n = ds, dl, fs and fl) sets,[15] designed for calculating the linear and non-linear electric properties of isolated systems and the interaction-induced electric properties of complexes. Among the LPol-*n* sets, the d-type basis sets (LPol-ds and LPol-dl) contain only first-order polarization functions (*i.e.*, d-type orbitals for the first row atoms), while the f-type bases (LPol-fs and LPol-fl) additionally include second-order polarization functions (*i.e.*, f-type orbitals for the first row atoms). The 's' and the 'l' in the names of the basis sets stand for 'small' and 'large', respectively. The difference between the 'small' and the 'large' basis sets is in the number of first- and second-order contracted GTOs. The size of LPol-*n* sets thus increases in the following order: LPol-ds < LPol-dl < LPol-fs < LPol-fl. Within the ZPol sets the reduction of basis set size does not imply a significant deterioration in the accuracy of the calculated molecular electric properties. The larger LPol sets have been shown to yield accurate values for the linear and non-linear electric properties of isolated systems[15] and hydrogen-bonded complexes.[17] The quality of the LPol-*n* sets has also been confirmed through specific optical rotation (OR) calculations for test organic molecules.[18]

As a continuation of the computational tests performed with LPol-*n* sets aiming at defining the regions of their applicability in molecular calculations, in the present project we evaluate the usefulness of the modified LPol-*n* sets in the description of He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar and Ne–Ar van der Waals complexes, and improve them accordingly. These complexes have been studied both from the experimental and the theoretical point of view. Here we cite the most accurate results available and refer to that work for further references. Within the experimental results, Ogilvie *et al.*[19,20] obtained potential functions for the fundamental electronic states of He_2, Ne_2, Ar_2, He–Ne, Kr_2 and Xe_2 dimers and the corresponding vibrational energies. Additionally, they presented empirical potentials for He–Ne, He–Ar and Ne–Ar van der Waals complexes obtained from spectroscopic results. Aziz *et al.* studied Ar–Ar[21] and Ne–Ne[22] complexes experimentally. On the theoretical side, in the three last decades these van der Waals complexes have been investigated on numerous occasions.[23–32] A CCSD(T)/daug-cc-pV5Z-33211 (where 33 211 denotes a set of 3s3p2d1f1g midbond functions) potential is available for the Ar–Ar complex.[31] In 1999 Cybulski *et al.*[33] calculated the fundamental state potential energy curves for He_2, Ne_2, Ar_2, He–Ne, He–Ar and Ne–Ar complexes. They used the CCSD(T) method and the aug-cc-pV5Z basis set extended using a set of 3s3p2d2f1g midbond functions. For each complex, with the exception of He_2, the frequencies of the vibrational and pure rotational transitions were presented. The best potential available for He–He is the extrapolated FCI/daug-cc-pV5Z-3321 from ref. 29, which was obtained after correcting FCI/daug-cc-pVTZ-3321 results using CCSD(T)/daug-cc-pVTZ-3321 CCSD(T)/daug-cc-pV5Z-3321 differences. A CCSD(T)/daug-cc-pV5Z-33211 potential was evaluated for the Ne–Ne complex in ref. 30 and used in the calculation of virial coefficients. Using the CCSD(T) method and the augmented correlation consistent sextuple zeta basis set (aug-cc-pV6Z) completed using a set of 3s3p2d1f1g midbond functions, López *et al.*[34] evaluated the interaction potentials of He–Ne, He–Ar and Ne–Ar dimers. In the same year, Hodges *et al.*[35] presented the potential energy curves and ro-vibrational energy levels for He–Ne, He–Ar and Ne–Ar. The potential energy curves were obtained using a perturbation-theory-based method and a new extrapolation method, both developed by them.

The present paper is organized as follows. In the next section the theoretical background of the generation of polarized basis sets is briefly outlined. In subsection IIA we give details of the generation of the MLPol atomic basis set, and in subsection IIB we discuss the bases for the dimers. In section III we give the potential functions to which the *ab initio* data are fitted. In section IV the potentials and the ro-vibrational spectra are compared to the theoretical and experimental data available. The work is summarized in the last section.

II Generation of polarized basis sets

The different bases with which the potentials have been evaluated have been selected from systematic basis set studies. In this section we explain the details of the generation of the basis sets, starting with the atomic basis sets in subsection IIA, and in subsection IIB we concentrate on the dimer bases.

The idea of polarized sets, developed over the years by Sadlej and co-workers, is based on a simple physical model of a harmonic oscillator perturbed by an external (oscillating) electric field. Polarized basis sets are obtained by adding the so-called polarization functions to some *initial* set of primitive Gaussian-type functions, and thus the quality of the resulting polarized basis set depends strongly on the quality of the initial set. Describing the subtle van der Waals interaction is very demanding and a careful choice of the initial basis set, which should correctly describe both the regions close to and far from the nuclei, is necessary.

In the absence of an electric field, $\mathbf{F} = \mathbf{0}$, the primitive GTO $G_{\mu,\alpha}$ is a function of the electron coordinate $\mathbf{r}$ and is fully

defined by the orbital exponent α_μ, the angular momentum quantum number l, and the GTO origin $\mathbf{R}_\mu(\mathbf{0})$. Electric field perturbation leads to field-dependent GTOs,

$$G_{\mu,\alpha}(\mathbf{r}, \mathbf{R}_\mu(\mathbf{0}), \alpha_\mu) \rightarrow G_{\mu,\alpha}(\mathbf{r}, \mathbf{R}_\mu(\mathbf{F}), \alpha_\mu). \quad (1)$$

The eigenvectors characterizing a given isolated atom can be written as a linear combination of unperturbed primitive GTOs

$$u(\mathbf{r};\mathbf{0}) = \sum_\mu c_\mu(\mathbf{0}) G_{\mu,\alpha}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu), \quad (2)$$

and those describing an atom in an external electric field can be written as a linear combination of electric-field-dependent primitive GTOs

$$u(\mathbf{r};\mathbf{F}) = \sum_\mu c_\mu(\mathbf{F}) G_{\mu,\alpha}(\mathbf{r};\mathbf{R}_\mu(\mathbf{F}),\alpha_\mu). \quad (3)$$

The latter eigenvectors are functions of the electric field through both the primitive GTOs and the contraction coefficients. The first-order perturbed function $u^{(1)}(\mathbf{r};\mathbf{0})$ (referred to as first-order polarization function) can be written as[11]

$$u^{(1)}(\mathbf{r};\mathbf{0}) \approx \sum_{n=1}^{\infty} b_n (f_{n-}^{(1)} + f_{n+}^{(1)}), \quad (4)$$

with

$$f_{n\pm}^{(1)} = \sum_\mu c_\mu(\mathbf{0}) \alpha_\mu^{-n+1\mp1/2} G_{\mu,l\pm1}(\mathbf{r};\mathbf{R}_\mu(\mathbf{0}),\alpha_\mu) \quad (5)$$

The polarization functions, eqn (4), added to the initial basis set $\{G_{\mu,\alpha}(\mathbf{r}, \mathbf{R}_\mu(\mathbf{0}), \alpha_\mu)\}$ have the same orbital exponents as the primitive GTOs entering the field-independent vector $u(\mathbf{r};\mathbf{0})$, and the contraction coefficients are obtained from the corresponding $c_\mu(\mathbf{0})$ coefficients of $u(\mathbf{r};\mathbf{0})$ through a simple scaling.

Analogously to previous work,[12–15] we have introduced additional approximations to reduce the size of the resulting polarized set. First of all, the initial set of functions is contracted, and the polarization functions are generated only for the so-called valence orbitals. Next, we make use of the fact that the f_{n-} contributions to the polarization functions are to a large extent accounted for in the initial set of functions, and thus can be neglected. In contrast to the LPol sets, out of the possible f_{n+} functions only one term is included. According to previous work on polarized sets,[11] the term corresponding to $n = 2$ yields the most important contribution to the electric polarizabilities. However, interaction energy calculations performed in the present study for testing van der Waals complexes (neon dimer) prove that there is no substantial difference between the energies obtained using polarized basis sets with polarization functions corresponding to $n = 2$ and energies obtained using $n = 1$, the latter results being slightly more accurate. Thus, we have decided to use the better performing f_{n+} term corresponding to $n = 1$ in the polarized basis sets developed for interaction energy calculations. In the case of electric property calculations, however, the set with the $n = 2$ term should yield more accurate results. Further reduction of the basis set size has been accomplished through an appropriate reduction in the number of primitive GTOs forming the polarization function. This approximation is justified by the fact that the $\alpha_\mu^{-n+1/2}$ scaling favors GTOs with small exponents, while the contraction coefficients for the large exponent GTOs become negligibly small. Additional flexibility in the polarized sets has been obtained through the addition of second-order polarization functions obtained using a method analogous to that used for the first-order functions, as described in detail in ref. 15. As in the case of the first-order functions, only the f_{n+} second-order term corresponding to $n = 1$ has been included in the polarized set.

A Atomic basis sets

Since the quality of the resulting polarized set depends on the primitive GTOs, in the present study polarized sets are developed using large source sets, namely the [10s] basis set developed by van Duijneveldt[36] for helium, the [18s13p] basis set developed by Partridge[37] for neon, and the [20s15p] set developed by Partridge[38] for argon. Further improvement in the description of the regions far from the nucleus and increased basis set flexibility are guaranteed by augmentation of the source set with diffuse functions. The orbital exponents of the additional diffuse functions are evaluated by the geometrical progression of the two most diffuse exponents in the source set. Thus the initial sets are of the form: He [11s], Ne [19s14p], and Ar [21s16p].

Choice of the initial set contraction scheme as well as the optimal number of primitive GTOs entering the first-order polarization function follows from careful finite-field atomic Hartree–Fock self consistent field (HF SCF) static polarizability calculations. The external static electric field strength is chosen to be equal to 0.001 au. The Hartree–Fock limit static polarizabilities reported by Kobus[39] are chosen as reference results. The GTOs corresponding to the initial set are contracted to the form [11s/5s] for He, [19s14p/7s6p] for Ne, and [21s16p/8s7p] for Ar, with the four most diffuse s-type primitives for He and the five most diffuse s- and p-type GTOs for Ne and Ar left uncontracted to ensure a high flexibility in the basis set. Next, the first- and second-order polarization functions corresponding to $n = 1$ are obtained using the procedure described in detail in ref. 15. The 6, 8, and 10 most diffuse GTOs are chosen to form the first-order polarization function in the He, Ne, and Ar MLPol sets, respectively. The number of primitive GTOs in the second-order polarization functions is reduced in the two functions with the largest exponents for He, and in the three with the largest exponents for Ne and Ar, which is justified by the fact that the scaling used in the polarization function generation favours diffuse GTOs over those with higher exponents. Amongst the polarization functions, the three most diffuse p- and the two most diffuse

Table 1 Ground-state HF SCF energies E_0 and finite-field static polarizabilities $\alpha(0)$ in atomic systems. All values are given in atomic units

	E_0		$\alpha(0)$		
System	ds, dl	ref. 39	ds	dl	ref. 39
He	−2.86167305	−2.861679995631	1.2982	1.3218	1.3222
Ne	−128.54709405	−128.547098109	2.3606	2.3754	2.3767
Ar	−526.81749019	−526.817512804	10.7214	10.7398	10.7580

d-type primitive GTOs in the case of He, and the four most diffuse d- and the three most diffuse f-type primitive GTOs for Ne and Ar are left uncontracted. Additionally, the d-type contraction for Ar is split into two functions. The final MLPol sets are thus of the form [11s6p4d/5s4p3d] for He, [19s14p8d5f/7s6p5d4f] for Ne, and [21s16p10d7f/8s7p6d4f] for Ar, and similarly to the LPol-*n* sets they are referred to as MLPol-fl sets. Additionally, three smaller polarized sets are obtained, namely MLPol-ds ([11s6p/4s3p] for He, [19s14p8d/6s5p4d] for Ne, [21s16p10d/7s6p5d] for Ar), MLPol-dl ([11s6p/5s4p] for He, [19s14p8d/7s6p5d] for Ne, [21s16p10d/8s7p6d] for Ar), and MLPol-fs ([11s6p4d/4s3p2d] for He, [19s14p8d5f/6s5p4d3f] for Ne, [21s16p10d7f/7s 6p5d3f] for Ar). Basis set exponents and contraction coefficients are reported in the ESI.† In the following, we denote the MLPol-*n* (n = ds, dl, fs, fl) bases as *n*.

The He, Ne, and Ar atomic Hartree–Fock ground-state energies and finite-field static electric polarizabilities were evaluated using Molcas 7.4[40] and reported in Table 1. From the point of view of further molecular applications, the differences between the ds and the dl results and the reference values are negligibly small for both energies and polarizabilities.

B Dimer basis sets

In order to carry out the basis set studies, we evaluated CCSD(T) interaction energies in each complex for the 13 internuclear geometries previously investigated by Cybulski and Toczyłowski.[33] Since our aim is the evaluation of the ro-vibrational spectra, we concentrate on the majority of the points within the potential well. The geometries are displayed in Table 2. We consider as a reference the most accurate results available of those obtained using Dunning's basis sets (errors of around 1%), namely those obtained with the doubly-augmented correlation-consistent polarized valence quintuple zeta basis set (daug-cc-pV5Z) of Dunning and co-workers extended using a set of 3s3p2d2f1g midbond functions[33] (denoted daV5Z-33221). The aim is to get for these 13 representative interaction energies, the rmse with respect to those obtained with the reference basis set as small as possible, keeping the total number of basis set functions smaller than in the reference set. In the case of the He–He dimer, we compare these results with the extrapolated FCI/daug-cc-pV5Z-3321 values in ref. 29. The differences between the two potentials are insignificant, and therefore in order to use the same reference for all the complexes, we decided to proceed considering only the daV5Z-33221 as reference results. In order to determine the accuracy of the new basis sets with respect to basis set size, we also take into account potentials evaluated with smaller Dunning's basis sets. In this way, for each of the investigated complexes we consider the xaug-cc-pVXZ (x = —, d; X = D, T, Q, 5) basis sets. To improve basis set efficiency, additional sets of midbond functions placed in the middle of the van der Waals bond are added to each basis set. We use the 3s3p2d2f1g set of functions (abbreviated as 33 221) by Cybulski *et al.*,[33] and the 3s3p2d1f1g set (denoted 33 211) by Fernández and Koch.[31] The differences in the results obtained with the 33 221 and the 33 211 sets are insignificant, therefore in general we only report the results corresponding to the 33 221 set of functions. Both sets of midbond functions as well as smaller sets, obtained by reducing the 33 211 set through subsequent removals of the most diffuse functions, are considered in the calculations carried out with the new implemented bases. Basis set exponents are not modified.

Table 2 Internuclear distances R selected for the basis set analysis. All values are in Å

He_2	Ne_2	Ar_2	HeNe	HeAr	NeAr
1.750	2.250	3.000	2.000	2.250	2.500
2.000	2.500	3.250	2.250	2.500	2.750
2.250	2.750	3.500	2.500	2.750	3.000
2.500	3.000	3.750	2.750	3.000	3.250
2.750	3.075	3.775	3.000	3.250	3.475
2.950	3.100	3.800	3.025	3.475	3.500
2.975	3.125	3.850	3.050	3.500	3.525
3.000	3.250	4.000	3.250	3.525	3.750
3.025	3.500	4.250	3.500	3.750	4.000
3.250	3.750	4.500	3.750	4.000	4.250
3.500	4.000	5.000	4.000	4.500	4.500
4.000	4.500	6.000	4.500	5.000	5.000
5.000	5.000	7.000	5.000	6.000	6.000

A summary of the main results, *i.e.* those significant in the result analysis, is given in Tables 3–8. We report the total number of basis set functions, the lowest *ab initio* interaction energy for each curve, and the root mean square error (rmse) for the set of points corresponding to the negative interaction energy region, evaluated with respect to the daV5Z-33221 potential taken as reference. Basis sets without midbond functions perform much worse than those extended, therefore we do not include the corresponding results in the Tables. The total set of interaction energies calculated for all 13 points using all reported basis sets can be obtained from the authors upon request.

From the analysis of the results, we can see that for the He–He complex the bases that give the best results with respect to a compromise between accuracy and basis set size are the ds-3321 (55 functions) within the MLPol bases, and the apc2-33221 (91 functions) within Jensen's. The former is about the same size as the aVDZ-33211 basis set (56 functions), and gives a lower rmse. The apc2-33221 is of the same size as the aVTZ-33221 basis set and yields a slightly smaller rmse.

For the Ne–Ne complex and after carrying out a similar analysis, we choose the fl-321 set (170 functions) within the MLPol, and the apc2-332 set (114 functions) within the apc2 sets. The former is comparable in size to the daVTZ-33221 basis set (169 functions, rmse of 0.66 cm^{-1}), but it reproduces the potential considerably better, giving an rmse of 0.25 cm^{-1}. It also performs slightly better than the aVTZ-33221 set.

Table 3 Basis set analysis for He_2. Symbol n denotes the number of basis functions; ΔE_{min} is the lowest CCSD(T) interaction energy within the set of 13 points used in the basis set analysis; rmse stands for the root mean square error for the points corresponding to negative interaction energies. Interaction energy and root mean square error values are in inverse centimetres. See text for basis set notation

Basis set	daV5Z-33221	aVDZ-33221	aVTZ-33221	aVQZ-33221	aV5Z-33221	daVDZ-33221	daVTZ-33221
n	255	63	91	137	205	71	109
ΔE_{min}	−7.40	−7.61	−7.35	−7.38	−7.39	−7.41	−7.41
rmse	0.00	0.16	0.07	0.03	0.01	0.14	0.04
Basis set	daVQZ-33221	apc2-33221	apc2-33211	apc2-3321	apc2-332	ds-33221	ds-33211
n	169	91	84	75	68	71	64
ΔE_{min}	−7.40	−7.44	−7.30	−7.28	−7.11	−8.06	−7.90
rmse	0.01	0.05	0.14	0.15	0.28	0.50	0.53
Basis set	ds-3321	ds-3311	ds-3221	ds-332	dl-33221	dl-33211	dl-3321
n	55	50	47	48	79	72	63
ΔE_{min}	−7.65	−8.19	−8.05	−7.10	−7.27	−7.17	−7.07
rmse	0.19	0.66	0.55	0.38	0.15	0.25	0.33
Basis set	dl-332	fs-33221	fs-33211	fs-3321	fs-332	fs-321	fs-331
n	56	91	84	75	68	60	63
ΔE_{min}	−6.81	−8.42	−9.64	−7.84	−7.45	−7.13	−7.18
rmse	0.55	0.81	1.80	0.36	0.27	0.32	0.26
Basis set	fs-322	fl-33221	fl-33211	fl-3321	fl-332		
n	65	109	102	93	86		
ΔE_{min}	−7.39	−7.38	−7.30	−7.28	−7.23		
rmse	0.30	0.09	0.14	0.16	0.19		

Table 4 Basis set analysis for Ne_2. See caption of Table 3 for details

Basis set	daV5Z-33221	aVDZ-33221	aVTZ-33221	aVQZ-33221	aV5Z-33221	daVDZ-33221	daVTZ-33221
n	371	91	137	205	299	109	169
ΔE_{min}	−28.71	−30.29	−29.04	−28.67	−28.66	−32.15	−29.55
rmse	0.00	1.35	0.28	0.04	0.04	2.51	0.66
Basis set	daVQZ-33221	apc2-33221	apc2-33211	apc2-3321	apc2-3311	apc2-3221	apc2-3211
n	255	137	130	121	116	118	113
ΔE_{min}	−28.80	−31.33	−29.78	−29.24	−28.71	−29.28	−28.52
rmse	0.07	1.86	0.88	0.49	0.29	0.53	0.30
Basis set	apc2-332	apc2-321	ds-33221	ds-33211	ds-3321	ds-332	ds-3221
n	114	106	127	120	111	104	108
ΔE_{min}	−28.75	−27.95	−36.47	−32.85	−28.79	−28.01	−28.28
rmse	0.29	0.65	5.88	3.17	0.60	0.61	0.70
Basis set	ds-3211	ds-3311	dl-33221	dl-33211	dl-3321	dl-332	fs-33221
n	103	106	145	138	129	122	169
ΔE_{min}	−27.48	−28.38	−28.91	−27.82	−27.30	−26.29	−46.55
rmse	1.09	0.64	0.37	0.76	1.12	1.89	11.53
Basis set	fs-33211	fs-3321	fs-332	fs-321	fs-331	fl-33221	fl-33211
n	162	153	146	138	141	201	194
ΔE_{min}	−38.27	−31.68	−30.37	−29.86	−30.23	−29.61	−29.23
rmse	6.79	2.21	1.26	1.05	1.17	0.78	0.52
Basis set	fl-3321	fl-332	fl-321	fl-331			
n	185	178	170	173			
ΔE_{min}	−28.82	−29.00	−28.71	−28.76			
rmse	0.28	0.28	0.25	0.25			

The fl-321 set gives better results than all of the apc2 basis sets, but it is also larger. The apc2-332 basis set shows a very good efficiency in terms of giving a low rmse and having a small number of basis functions. The error is considerably lower than that obtained with the larger daVTZ-33221 basis set, and comparable to that of the aVTZ-33221 basis set. Therefore, we decided to run the whole potential also with this basis set.

For the Ar–Ar complex, we select the fl-3321 (203 functions), and the apc2-33211 (138 functions) bases. The former is the

Table 5 Basis set analysis for Ar_2. See caption of Table 3 for details

Basis set	daV5Z-33221	aVDZ-33221	aVTZ-33221	aVQZ-33221	aV5Z-33221	daVDZ-33221	daVTZ-33221
n	379	99	145	213	307	117	177
ΔE_{min}	−97.33	−112.97	−99.47	−96.46	−96.97	−115.50	−100.29
rmse	0.00	11.21	1.69	0.86	0.30	12.95	2.21
Basis set	daVQZ-33221	apc2-33221	apc2-33211	apc2-3321	apc2-332	ds-3321	ds-3221
n	263	145	138	129	122	129	126
ΔE_{min}	−97.07	−99.00	−98.40	−96.15	−92.27	−98.89	−96.36
rmse	0.48	1.75	1.65	2.22	4.86	2.12	2.69
Basis set	ds-332	dl-33211	dl-3321	fl-33211	fl-3321	fl-3311	fl-3221
n	122	156	147	212	203	198	200
ΔE_{min}	−87.72	−101.85	−95.52	−99.09	−97.42	−96.32	−97.13
rmse	9.43	4.00	3.20	1.73	1.40	2.00	1.46
Basis set	fl-3211	fl-332					
n	195	196					
ΔE_{min}	−95.97	−94.52					
rmse	2.17	3.07					

Table 6 Basis set analysis for He–Ne. See caption of Table 3 for details

Basis set	daV5Z-33221	aVDZ-33221	aVTZ-33221	aVQZ-33221	aV5Z-33221	daVDZ-33221	daVTZ-33221
n	313	77	114	171	252	90	139
ΔE_{min}	−14.64	−15.33	−14.57	−14.59	−14.61	−15.80	−14.72
rmse	0.00	0.58	0.14	0.07	0.02	0.84	0.14
Basis set	daVQZ-33221	apc2-33221	apc2-33211	apc2-32211	apc2-3321	apc2-332	ds-33211
n	212	114	107	104	98	91	92
ΔE_{min}	−14.65	−15.15	−14.57	−14.59	−14.37	−14.09	−16.18
rmse	0.04	0.33	0.35	0.35	0.41	0.60	1.11
Basis set	ds-3321	ds-3221	ds-332	dl-33211	dl-3321	dl-332	fs-3321
n	83	80	76	105	96	89	114
ΔE_{min}	−15.19	−15.13	−13.89	−14.17	−13.94	−13.40	−15.43
rmse	0.54	0.54	0.93	0.65	0.79	1.20	0.75
Basis set	fs-332	fs-331	fs-322	fs-321	fl-33221	fl-33211	fl-3321
n	107	102	104	99	155	148	139
ΔE_{min}	−14.85	−14.81	−15.06	−14.89	−14.70	−14.59	−14.53
rmse	0.37	0.29	0.41	0.35	0.24	0.32	0.34

one that gives the best results within the MLPol bases, resulting in a region around the potential minimum closer to the daV5Z-33221 results than that showed by the daVQZ-33221 basis set (263 functions). The apc2-33211 basis set has only 138 functions and gives better results than Dunning's aVTZ-33221 (145 functions) and daVTZ-33221 (177 functions) bases.

For the evaluation of the interaction potential energy curve in the He–Ne system, the fs-331 (102 functions) and the apc2-3321 (98 functions) sets were selected. Both are smaller than the aVTZ-33221 set, and yield rmses of 0.29 and 0.41 cm^{-1}, respectively.

The best choices for the He–Ar complex from the point of view of compromise between accuracy and computing cost are the ds-3321 (92 functions) among the MLPol and the apc2-33211 (111 functions) among the apc2 sets. Both these bases are somewhat smaller than the aVTZ-33221 set and describe the interaction energies similarly well yielding rmses of 0.55 and 0.41 cm^{-1}.

For Ne–Ar, the apc2-3321 basis (125 functions) is chosen. It is smaller than the aVTZ-33221 set and yields a minimum interaction energy value closer to that obtained with the daV5Z-33221 set. Additionally, we select the ds-3321 set (120 functions) which is the best basis among the MLPol sets from the point of view of a compromise between the accuracy of results and the basis set size.

The interaction energies are evaluated using the CCSD(T) method and the selected basis sets for 60 internuclear distances, taken between 1.750 and 5.000 Å, 2.250 and 7.000 Å, 3.000 and 9.000 Å, 2.000 and 5.500 Å, 2.250 and 6.500 Å, and 2.500 and 6.500 Å, for the He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar, and the Ne–Ar complexes, respectively. Additionally, the daV5Z-33221 interaction energies are calculated for all complexes. All interaction energy calculations are carried out with the DALTON 2.0 package.[41] We keep the core frozen and correct for the basis set superposition error using the counterpoise method.[42] Interaction energies are reported in cm^{-1} and distances in Å. The whole set of results is given in the ESI.†

Table 7 Basis set analysis for He–Ar. See caption of Table 3 for details

Basis set	daV5Z-33221	aVDZ-33221	aVTZ-33221	aVQZ-33221	daVDZ-33221	daVTZ-33221	
n	317	81	118	175	94	143	
ΔE_{min}	−20.70	−22.07	−20.61	−20.55	−22.18	−20.77	
rmse	0.00	1.01	0.25	0.14	1.09	0.19	
Basis set	daVQZ-33221	apc2-33221	apc2-33211	apc2-3321	apc2-3221	apc2-3211	apc2-3311
n	216	118	111	102	99	94	97
ΔE_{min}	−20.65	−20.59	−20.53	−20.10	−20.22	−20.12	−19.89
rmse	0.08	0.33	0.41	0.67	0.57	0.71	0.88
Basis set	apc2-332	ds-33221	ds-33211	ds-3321	ds-332	dl-33221	dl-33211
n	95	108	101	92	85	121	114
ΔE_{min}	−19.45	−22.35	−21.99	−20.62	−18.68	−21.10	−20.46
rmse	1.19	1.18	1.22	0.55	1.98	0.43	0.62
Basis set	dl-3321	dl-332	fs-33221	fs-33211	fs-3321	fs-3221	fs-3211
n	105	98	139	132	123	120	115
ΔE_{min}	−19.76	−18.45	−22.87	−23.48	−21.28	−21.32	−21.35
rmse	1.05	2.14	1.55	2.09	0.66	0.64	0.53
Basis set	fs-3311	fs-332	fs-331	fl-33221	fl-33211	fl-3321	fl-332
n	118	116	111	164	157	148	141
ΔE_{min}	−21.31	−20.32	−19.68	−20.62	−20.46	−20.37	−20.13
rmse	0.51	0.67	1.10	0.32	0.45	0.50	0.67

Table 8 Basis set analysis for Ne–Ar. See caption of Table 3 for details

Basis set	daV5Z-33221	aVDZ-33221	aVTZ-33221	aVQZ-33221	daVDZ-33221	daVTZ-33221	
n	375	95	141	209	113	173	
ΔE_{min}	−45.33	−49.95	−45.46	−45.07	−50.67	−46.81	
rmse	0.00	3.36	0.41	0.27	4.19	1.10	
Basis set	daVQZ-33221	apc2-33221	apc2-33211	apc2-3321	apc2-3221	apc2-3311	apc2-3211
n	259	141	134	125	122	120	117
ΔE_{min}	−45.39	−46.70	−46.05	−45.26	−44.88	−44.40	−44.26
rmse	0.14	0.97	0.83	0.78	0.91	1.35	1.34
Basis set	apc2-332	ds-33211	ds-3321	ds-3221	ds-3311	ds-3211	dl-33221
n	118	129	120	117	115	112	154
ΔE_{min}	−44.26	−47.93	−45.07	−44.76	−43.59	−43.25	−47.28
rmse	1.38	2.20	1.48	1.67	2.56	2.85	1.51
Basis set	dl-33211	dl-3321	fs-3321	fs-332	fs-331	fs-321	fl-33211
n	147	138	162	155	150	147	203
ΔE_{min}	−45.49	−43.57	−49.24	−46.68	−44.50	−44.42	−46.15
rmse	1.31	2.07	2.62	1.31	1.34	1.29	0.83
Basis set	fl-3321	fl-3221	fl-3311	fl-3211	fl-332		
n	194	191	189	186	187		
ΔE_{min}	−45.32	−45.27	−44.94	−44.89	−44.84		
rmse	0.68	0.69	0.84	0.86	0.89		

III Potential functions

In order to fit the interaction energies we use two different analytic potential functions. For the He–He and Ne–Ne dimers the one reported by Aziz *et al.*,[43]

$$V(R) = \frac{\varepsilon}{K_B} V^*(Ra_0/r_m) \tag{6}$$

$$V^*(r) = A^* e^{-\alpha^* r + \beta^* r^2} - F(r) \sum_{n=0}^{2} \frac{C_{6+2n}}{r^{6+2n}}, \tag{7}$$

where $F(r)$ takes the values:

$$F(r) = \begin{cases} \exp(-(D/r-1)^2) & \text{for } r \le D \\ 1 & \text{for } r \ge D \end{cases} \tag{8}$$

and ε/K_B, α^*, β^*, r_m, c_6, c_8 and c_{10} are adjustable parameters. The multiplicative constants A^* and D for each complex are taken from Aziz's results,[43] and a_0 is the Bohr radious with a value of 0.529177249 Å.

In the case of Ar–Ar complex we use the potential from ref. 21,

$$V(R) = \frac{\varepsilon}{K_B} V^*(R) \tag{9}$$

$$V^*(R) = A^* \exp\left(-\alpha^* \frac{Ra_0}{r_m} + \beta^* \left(\frac{Ra_0}{r_m}\right)^2\right) - f(\rho R) \sum_{n=0}^{2} \frac{C_{6+2n}}{(Ra_0/r_m)^{6+2n}} g_{6+2n}(\rho R), \tag{10}$$

where $g_n(x)$ and $f(x)$ are given by

$$g_n(x) = (1 - \exp(-2.1x/n - 0.109x^2/\sqrt{n}))^n \tag{11}$$

$$f(x) = 1 - x^{1.68} e^{-0.78x} \tag{12}$$

with A^*, α^*, β^*, r_m, c_6, c_8 and c_{10} being adjustable parameters. The values for ε/K_B and ρ are taken from ref. 21.

In the case of the heteronuclear dimers we use the potential function reported by Korona *et al.*,[44]

$$V(R) = Ae^{-\alpha R + \beta R^2} - \sum_{n=3}^{8} f_{2n}(R, b) c_{2n}/R^{2n}, \tag{13}$$

with f_{2n}(R, b):

$$f_{2n}(R, b) = 1 - e^{-bR} - \sum_{k=0}^{2n} (bR)^k/k!, \tag{14}$$

where A, α, β, b, c_6, c_8, c_{10}, c_{12}, c_{14} and c_{16} are adjustable parameters.

The resulting potentials were used in the evaluation of the ro-vibrational spectra carried out with the LEVEL program.[45] The conversion factors used were a_0 = 0.529177249 Å and 1 Hartree = 219474.631 cm^{-1}.

IV Results and discussion

The interaction energies obtained for 60 interatomic distances with the selected bases were fitted to the potential functions presented in section III, and the corresponding ro-vibrational spectra were evaluated. The discussion of the results is centred in the comparison of the different potentials obtained with those previously available, and that of the theoretical spectroscopic results with their experimental counterparts.

The final parameters fitted to the *ab initio* points of the investigated potentials are presented in Tables 9 and 10. In all cases, limiting the study to potential points in the bound regions, we obtain rmses lower than 0.055 cm^{-1}. The particular values and the maximum errors for each potential are presented in Tables 11 and 12, where the geometries corresponding to the maximum errors are also reported. A single minimum is observed in all cases and the corresponding geometries (R_e) and energies (D_e) are given in the Tables.

Table 9 Parameters of the analytic interaction potential energy curves fitted to the *ab initio* energies obtained for the He–He, Ne–Ne, and Ar–Ar complexes with the CCSD(T) method and the selected basis sets. The numerical values of the parameters (r_m in Å, and ε/K_B in K) are given for R in au and the potential energy in K

He–He			
Parameter	daV5Z-33221	ds-3321	apc2-33221
A^*	186924.404	186924.404	186924.404
α^*	9.4738	8.6745	9.2766
β^*	−1.7949	−2.1178	−1.6712
c_6	2.6338	4.1720	2.9385
c_8	0.51984	−0.68267	0.755400
c_{10}	0.40565	1.5453	0.50177
r_m	2.7246	2.6809	2.6719
D	1.4380	1.4380	1.4380
ε/K_B	9.8339	8.0560	9.7474
Ne–Ne			
Parameter	daV5Z-33221	fl-321	apc2-332
A^*	895717.95	895717.95	895717.95
α^*	13.565	11.885	11.846
β^*	−0.99877	−0.021227	−0.06571
c_6	1.4995	2.5712	3.1346
c_8	−0.59396	7.8990	0.32144
c_{10}	1.2342	−5.9192	2.3529
r_m	3.4086	2.6481	2.6960
D	1.36	1.36	1.36
ε/K_B	22.267	35.164	42.203
Ar–Ar			
Parameter	daV5Z-33221	fl-3321	apc2-33211
A^*	160750	159630	219370
α^*	8.6548	10.112	11.015
β^*	−1.3740	−1.1766	−0.53331
c_6	2.8801	1.7048	1.4987
c_8	1.8787	−1.4317	−1.0789
c_{10}	3.1950	3.6510	3.6735
r_m	3.1694	3.1694	3.1694
ε/K_B	143.235	143.235	143.235
ρ	1.107	1.107	1.107

Considering the experimental results available, for the He–He complex we compare these to the empirical potential results from ref. 19. We also report these values for the Ne–Ne and the Ar–Ar complexes in order to show their performance with respect to the other accurate experimental data available for these complexes.[21,22,46] The differences are insignificant and within the error limits of our calculations. For the heteronuclear dimers we take as reference the experimental work in ref. 20.

For the homonuclear dimers when comparing the *ab initio* results to experiment, we can see in general an overestimation of the equilibrium distance and an underestimation of the interaction energy in the minima, giving the theoretical calculations weaker van der Waals bonds. For the He–He interaction energy the ds-3321 basis set gives better results, both with respect to the FCI extrapolated values of ref. 29 and to the empirical data. In the case of the Ne–Ne complex the best estimations are obtained with the apc2-332 basis set, and the differences among all the results are within the expected errors. The two new basis sets for the Ar–Ar complex give interaction energies closer to the experimental results

Table 10 Parameters of the analytic IPES fitted to the *ab initio* energies obtained for the He–Ne, He–Ar, and Ne–Ar complexes with the CCSD(T) method and the selected basis sets. Atomic units.

He–Ne			
Parameter	daV5Z-33221	fs-331	apc2-3321
A	24.392815	24.392432	24.392477
α	2.067199	2.050082	2.064146
β	−0.031019	−0.033150	−0.030539
b	2.593455	2.597176	2.596278
c_6	3.062315	3.097504	3.076422
$c_8 \times 10^{-2}$	0.316798	0.316806	0.316801
$c_{10} \times 10^{-3}$	0.427731	0.427731	0.427731
$c_{12} \times 10^{-4}$	0.772516	0.772516	0.772516
$c_{14} \times 10^{-6}$	0.181945	0.181945	0.181945
$c_{16} \times 10^{-8}$	0.054401	0.054401	0.054401
He–Ar			
Parameter	daV5Z-33221	ds-3321	apc2-33211
A	23.035005	23.030129	23.030147
α	1.629613	1.620589	1.629231
β	−0.046956	−0.045500	−0.045091
b	1.624366	1.686394	1.660555
c_6	9.432550	9.423011	9.415889
$c_8 \times 10^{-2}$	1.65523310	1.65523250	1.65523140
$c_{10} \times 10^{-3}$	3.797158	3.797158	3.797158
$c_{12} \times 10^{-4}$	1.165180	1.16518	1.16518
$c_{14} \times 10^{-6}$	4.66258	4.662580	4.662580
$c_{16} \times 10^{-8}$	2.36861000	2.36861000	2.36861000
Ne–Ar			
Parameter	daV5Z-33221	ds-3321	apc2-3321
A	75.461291	75.460886	75.461121
α	1.752350	1.753584	1.747095
β	−0.035990	−0.031267	−0.034637
b	1.641153	1.746640	1.689226
c_6	19.011752	19.021010	19.013500
$c_8 \times 10^{-2}$	3.928627	3.928629	3.928627
$c_{10} \times 10^{-3}$	10.562701	10.562701	10.562701
$c_{12} \times 10^{-4}$	37.987900	37.987900	37.987900
$c_{14} \times 10^{-6}$	17.816000	17.816000	17.816000
$c_{16} \times 10^{-8}$	10.607500	10.607500	10.607500

than the daV5Z-33221 basis set. This also holds for the majority of the MLPol bases we selected. Within the latter bases the fl- perform slightly better than the ds-. In the case of the heteronuclear complexes, the ds-3321 basis set gives results close to the apc2- bases, but not in all cases closer to experiment than the daV5Z-33221 results. For the He–Ne complex the fs-331 basis set provides an interaction energy that is in better agreement than the apc2-3321 with respect to the experimental value, but the former basis set is also considerably larger than the latter. In the determination of the dissociation energies, the apc2- bases show to perform in a very efficient way when combined with the right set of midbond functions.

In Tables 13 and 14 the ro-vibrational energy levels of the complexes are given, evaluated from the selected basis set potentials. Results are compared to the reference potential values and experiment. For the Ne–Ne complex the differences with respect to the reference and to the experimental values are lower for the fl-321 basis set, but the differences between these results and the apc2-332 are

Table 11 The rmse and maximum errors in cm^{-1} (interatomic distance R, and energy given for the latter), and the absolute minimum for the He–He, Ne–Ne, and Ar–Ar IPESs (R values in Å, energies in cm^{-1})

Basis set	rmse	max. error (R;E)	R_e	D_e
He–He				
FCIext.[29]			2.9699	7.629
daV5Z-33221	0.004	0.022 (2.000;376.6)	2.976	7.40
ds-3321	0.009	0.037 (2.000;389.2)	2.979	7.65
apc2-33221	0.011	0.038 (2.000;381.9)	2.979	7.44
Emp.[19]	—	—	2.9695	7.6245
Ne–Ne				
daV5Z-33221	0.006	0.020 (2.450;230.3)	3.098	28.71
fl-321	0.053	0.156 (2.500;174.3)	3.113	28.69
apc2-332	0.045	0.106 (2.500;172.7)	3.111	28.75
Exp.[22]	—	—	3.091	29.36
Emp.[19]	—	—	3.091	29.365
Ar–Ar				
daV5Z-33221	0.014	0.075 (5.500;−14.5)	3.778	97.34
fl-3321	0.040	0.116 (3.150;287.9)	3.791	97.42
apc2-33211	0.029	0.108 (3.150;289.5)	3.793	98.42
Exp.[21]	—	—	3.75	99.5539
Exp.[46]	—	—	3.761(3)	99.2(10)
Emp.[19]	—	—	3.7565	99.545

Table 12 The rmse and maximum errors in cm^{-1} (interatomic distance R, and energy given for the latter), and the absolute minimum for the He–Ne, He–Ar, and Ne–Ar IPESs (R values in Å, energies in cm^{-1})

Basis set	rmse $\times 10^4$	max. err.(R; E)	R_e	D_e
He–Ne				
daV5Z-33221	6.994	0.515 (2.350;139.9)	3.028	14.62
fs-331	6.017	0.835 (2.350;149.4)	3.040	14.46
apc2-3321	1.672	0.309 (2.150;452.2)	3.042	14.25
Emp.[20]			3.0309	14.384
He–Ar				
daV5Z-33221	1.844	0.438 (2.625;323.5)	3.492	20.68
ds-3321	6.108	0.812 (2.625;349.7)	3.513	20.26
apc2-33211	3.863	0.624 (2.625;338.8)	3.509	20.27
Emp.[20]			3.4804	20.104
Ne–Ar				
daV5Z-33221	1.146	0.303 (2.750;384.3)	3.493	45.33
ds-3321	8.086	0.605 (3.700;−41.6)	3.517	44.37
apc2-3221	4.482	0.501 (2.750;407.8)	3.505	44.97
Emp.[20]			3.4889	46.977

within the error limit we can expect in our calculations. For the Ar–Ar complex the fl-3321 and the apc2-33211 results are almost identical, being the latter sligthly closer to experiment. In the case of the heteronuclear dimers both the MLPol- and the apc2- bases give very similar values for the ro-vibrational transitions, that are close to the daV5Z-33221 and the experimental results. For the energy levels the apc2- values agree slightly better with the daV5Z-33221 results than the ds- values, and in He–Ne the fs- give better agreement than the apc2- results.

Table 13 Ne–Ne and Ar–Ar spectroscopic results. Energies in cm^{-1}. See text for basis set notation

Ne–Ne					
Basis set	$v = 0 \rightarrow 1$	$v = 0; J = 0 \rightarrow 1$	$E(0.0)$	$E(1.0)$	
daV5Z-33221	13.52	0.31	−16.34	−2.82	
fl-321	13.52	0.31	−16.37	−2.84	
apc2-332	13.48	0.31	−16.44	−2.96	
Emp.	13.840 ± 0.034[19]	0.34[47]	−16.3[22]	—	
Ar–Ar					
$\Delta G_{v+1/2}$ v''	daV5Z-33221	fl-3321	apc2-33211	Exp.[46]	
0	25.32	25.35	25.35	25.69(1)	
1	20.15	20.19	20.33	20.58(2)	
2	15.19	15.22	15.50	15.58(2)	
3	10.63	10.61	10.90	10.91(3)	
4	6.57	6.58	6.75	6.84(7)	
$J \rightarrow J'$	daV5Z-33221	fl-3321	apc2-33211	Exp.[48]	Exp.[46]
0–2	0.37	0.34	0.34	0.35	0.32
2–4	0.80	0.79	0.79	0.81	0.71
4–6	1.25	1.25	1.25	1.27	1.36
6–8	1.71	1.70	1.70	1.72	1.61
8–10	2.16	2.15	2.15	2.19	2.16
10–12	2.61	2.59	2.60	2.65	2.59
12–14	3.06	3.04	3.04	3.09	3.08
14–16	3.51	3.48	3.48	3.55	3.56
16–18	3.95	3.92	3.92	4.00	3.97
18–20	4.39	4.36	4.36	4.44	4.43
20–22	4.82	4.79	4.80	4.88	4.88
22–23	2.57	2.56	2.56	5.31	5.22

Table 14 He–Ne, He–Ar, and Ne–Ar spectroscopic results. Energies in [cm^{-1}]. See text for basis set notation

He–Ne							
Basis set	$v = 0; J = 0 \rightarrow 1$	$v = 0; J = 1 \rightarrow 2$	$E(0.0)$				
daV5Z-33221	0.71	1.35	−2.59				
fs-331	0.70	1.34	−2.66				
apc2-3321	0.70	1.33	−2.49				
Emp.[20]	0.706 ± 0.033	1.348 ± 0.039	—				
He–Ar							
Basis set	$v = 0; J = 0 \rightarrow 1$	$v = 0; J = 1 \rightarrow 2$	$v = 0; J = 2 \rightarrow 3$	$E(0.0)$			
daV5Z-33221	0.58	1.17	1.71	−7.05			
ds-3321	0.58	1.15	1.70	−6.79			
apc2-33211	0.58	1.16	1.70	−6.95			
Emp.[20]	0.5897 ± 0.0085	1.1670 ± 0.0093	1.717 ± 0.011				
Ne–Ar							
Basis set	$v = 0; J = 0 \rightarrow 1$	$v = 0; J = 1 \rightarrow 2$	$v = 0; J = 2 \rightarrow 3$	$E(0.0)$	$E(1.0)$	$E(2.0)$	$E(3.0)$
daV5Z-33221	0.19	0.38	0.58	−32.60	−14.11	−4.05	−0.27
ds-3321	0.19	0.38	0.57	−32.40	−13.81	−3.88	−0.20
apc2-332	0.19	0.38	0.57	−32.58	−14.11	−4.04	−0.27
Emp.[20]	0.19405 ± 0.00049	0.38792 ± 0.00049	0.58133 ± 0.00053	−32.8905[49]			

V Summary and conclusions

We have derived new efficient basis sets for the evaluation of interaction energies in the He–He, Ne–Ne, Ar–Ar, He–Ne, He–Ar and Ne–Ar van der Waals complexes. To this end we carried out systematic basis set studies taking as starting point the MLPol-*n* and Jensen's aug-pc-2 basis sets. The quality of the new MLPol sets was first tested through finite-field Hartree–Fock atomic polarizability calculations. For each complex we carried out 13 CCSD(T) interaction energy calculations using each of the new bases, and selected the best basis set taking as reference CCSD(T)/daV5Z-33221 values. Extension of the bases with different sets of midbond functions was considered. With the selected bases we obtained the potentials and tested them further by evaluating the ro-vibrational spectra of the complexes. The results showed good performance for the

new bases, as they were in general in better agreement with the available experimental data than those provided by the daV5Z-33221 basis sets. Work on the extension to larger van der Waals complexes is in progress.

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