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Coupled cluster calculations of the ground state potential and interaction induced electric properties of the mixed dimers of helium, neon and argon

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Using augmented polarized correlation consistent basis sets extended with midbond functions, we evaluate the ground state interaction potential and the induced electric dipole polarizabilities and first and second hyperpolarizabilities of the He–Ar, Ne–Ar and He–Ne van der Waals complexes. For the calculation of the potential we resort to the coupled cluster singles and doubles (CCSD) model corrected for triple excitations, CCSD(T), whereas properties are evaluated with CCSD response theory. As a check of the quality of the potential, the rovibrational spectrum and the gas second virial coefficients are evaluated. The rovibrational spectra improve previously available theoretical results, although the dissociation energies are probably still slightly underestimated. For the gas second virial coefficients the agreement with experiment is satisfactory. The frequency dependence of the interaction (hyper)polarizabilities is analysed and a comparison with previous results on the mixed dimers and the pure gases is made.

1. Introduction

Interest in the field of nonlinear optics has grown continuously since its origins in 1961 with the observation of second harmonic generation by Franken *et al.* [1]. Nowadays nonlinear optical effects play an important role in many optical devices, with applications ranging from communications to medicine. Accurate theoretical determination of frequency-dependent polarizabilities and hyperpolarizabilities of molecules is important for the description of nonlinear optical experiments, and it has recently become possible using response function theory. Not only high electron correlated methods but also large basis sets are required to obtain results that compare well with experiment and have predictive power.

In previous work [2–5] we evaluated accurate gas and (hyper)polarizability second virial coefficients of helium, neon and argon gases. These coefficients account for the influence of two-body interactions in the analysis of the pressure dependence of the properties. In general, the results obtained were more reliable than the available experimental data, which often carry large uncertainties and differ quite considerably from one experiment to another. Accurate *ab initio* results are thus very useful as test and guidance to the experimental work. Here we extend these studies to heteronuclear dimers, that is He–Ar, Ne–Ar and He–Ne. In contrast to homonuclear dimers, these complexes have no inversion centre and thus the van der Waals interaction also induces dipole moments and first hyperpolarizabilities. These give rise to additional contributions to the pressure dependence of the electrical and optical properties of gas mixtures, which are not present for the pure gases.

The van der Waals complexes HeAr, NeAr and HeNe have been investigated in a number of studies in recent years [6–13], most of them focused on the

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potential energy curves and the rovibrational spectra. Few references report interaction-induced properties for some selected points [10, 11]. In the present article we report accurate *ab initio* calculations not only for the interaction potentials but also for the interaction-induced dipole moments and (hyper)polarizabilities for a wide range of internuclear distances, as needed for the evaluation of virial coefficients. In a separate study we will determine the virial coefficients of the gas mixtures for various optical processes [14]. From the experimental point of view, on these mixed van der Waals systems there is a considerable lack of information in the literature. Therefore predictiveness is our goal, also in view of the high accuracy of the presented calculations, in the hope that the results will stimulate further experimental work.

2. Computational details

For a heteronuclear (*A–B*) dimer the interaction contribution ΔP to a general extensive property P (the symbol Δ is employed throughout to indicate 'interaction-induced') is obtained as

$$\Delta P(R) = P_{A-B}(S_{A-B}|R) - P_A(S_{A-B}|R) - P_B(S_{A-B}|R), \quad (1)$$

where $P_{A-B}(S_{A-B}|R)$ is the property of the dimer evaluated in the dimer basis set S_{A-B} at the interatomic distance R and $P_A(S_{A-B}|R)$ ($P_B(S_{A-B}|R)$) the property of the monomer A (B) evaluated in the dimer basis set at the same geometry. The counterpoise correction proposed by Boys and Bernardi [15] is employed to account for basis set superposition errors.

The ground state intermolecular potentials $V(R)$ are evaluated using CCSD(T) and the aug-cc-pV6Z-33211 basis set. [16, 17]. The midbond functions are located in the middle of the van der Waals bond and their exponents can be found in [18]. These functions are known to improve, in general, the efficiency of the basis set and this effect is almost independent of their location along the van der Waals bond [19, 20]. The values of the potentials for selected geometries are given in table 1. Here and in all following calculations the occupation of the core orbitals (1*s* in Ne and 1*s*, 2*s* and 2*p* in Ar) is kept frozen.

In order to evaluate the interaction-induced dipole moment and (hyper)polarizabilities, we used an approach similar to that adopted in our previous work on helium, neon and argon [2–5]. For the (hyper)polarizabilities in particular we consider the frequency dependence up to second order by expanding the properties in terms of the Cauchy moments, $\Delta S(-4)$,

Table 1. He–Ne, He–Ar and Ne–Ar ground state electronic potentials $V(R)$ μE_h calculated at the CCSD(T)/aug-cc-pV6Z-33211 level.

R/au	He–Ne	R/au	He–Ar	R/au	Ne–Ar
3.75	4652.3159	4.25	8089.6801	4.75	5870.2449
4.25	1161.0852	4.75	2519.3104	5.25	1482.5734
4.75	194.3348	5.25	641.2364	5.75	156.1510
5.00	35.8377	5.75	64.9646	6.00	−71.2144
5.25	−35.0111	6.00	−34.8179	6.25	−171.3439
5.50	−61.4825	6.25	−78.9826	6.50	−203.7993
5.65	−66.1552	6.50	−93.3486	6.65	−205.4842
5.75	−66.5520	6.65	−94.0819	6.75	−202.1819
5.85	−65.4959	6.75	−92.5964	7.00	−185.0246
6.00	−62.1448	7.00	−84.9810	7.50	−138.8056
6.50	−45.7368	7.50	−63.6145	8.00	−98.0725
7.00	−31.0195	8.50	−31.8675	8.50	−68.2407
7.50	−20.6777	9.50	−15.8682	9.50	−33.7042
8.00	−13.8840	10.50	−8.3894	10.50	−17.6746
9.00	−6.6048	11.50	−4.7537	11.50	−9.8666
10.00	−3.3983	13.00	−2.1793	13.00	−4.5419
12.00	−1.0907	15.00	−0.8969	15.00	−1.8604
14.00	−0.4235	16.00	−0.6028	16.00	−1.2484
16.00	−0.1882	18.00	−0.2932	17.00	−0.8598
17.00	−0.1305	19.00	−0.2108	18.00	−0.6057
18.00	−0.0926	20.00	−0.1541	19.00	−0.4351
19.00	−0.0669			20.00	−0.3187
20.00	−0.0491				

and the hyperpolarizability dispersion coefficients, $\Delta(\beta_{||}\times A)$, $\Delta\beta_K(2)$, $\Delta(\gamma_{||}\times A)$, and $\Delta D_K(2)$ [21–23],

$$\Delta\alpha(-\omega;\omega)=\Delta\alpha+\omega^2\Delta S(-4)+\mathcal{O}(\omega^4), \quad (2)$$

$$\Delta\beta_{||}(-\omega_0;\omega_1,\omega_2)=\Delta\beta_{||}+\omega_L^2\,\Delta(\beta_{||}\times A)+\mathcal{O}(\omega_i^4), \quad (3)$$

$$\Delta\beta_K(-\omega;\omega,0)=\Delta\beta_{||}+2\omega^2\Delta\beta_K(2)+\mathcal{O}(\omega^4), \quad (4)$$

$$\Delta\gamma_{||}(-\omega_0;\omega_1,\omega_2,\omega_3)=\Delta\gamma_{||}+\omega_L^2\,\Delta(\gamma_{||}\times A)+\mathcal{O}(\omega_i^4), \quad (5)$$

$$\Delta\gamma_K(-\omega;0,0,\omega)=\Delta\gamma_{||}+2\omega^2\Delta D_K(2)+\mathcal{O}(\omega^4), \quad (6)$$

where $\omega_L^2=\sum_{i=0}^{n}(\omega_i^2)$, with $n=2$ for $\Delta\beta_{||}$ and $n=3$ for $\Delta\gamma_{||}$. Above α stands for both the average and the anisotropy of the electric dipole polarizability. These are defined as (frequency dependence neglected for conciseness, and axis z chosen parallel to the internuclear axis)

$$\alpha_{ave}=\frac{1}{3}(2\alpha_{xx}+\alpha_{zz}), \quad (7)$$

$$\alpha_{ani}=\alpha_{zz}-\alpha_{xx}. \quad (8)$$

Also

$$\beta_{||}=\frac{1}{5}\sum_{\xi}(\beta_{z\xi\xi}+\beta_{\xi z\xi}+\beta_{\xi\xi z}), \quad (9)$$

$$\beta_K=\frac{3}{2}(\beta_{||}-\beta_{\perp})=\frac{3}{10}\sum_{\xi}(4\beta_{\xi z\xi}-\beta_{z\xi\xi}-\beta_{\xi\xi z}), \quad (10)$$

$$\gamma_{||}=\frac{1}{15}\sum_{\xi}\sum_{\eta}(\gamma_{\xi\xi\eta\eta}+\gamma_{\xi\eta\xi\eta}+\gamma_{\xi\eta\eta\xi}), \quad (11)$$

$$\gamma_K=\frac{3}{2}(\gamma_{||}-\gamma_{\perp})=\frac{1}{10}\sum_{\xi}(4\gamma_{\xi\eta\xi\eta}-\gamma_{\xi\xi\eta\eta}-\gamma_{\xi\eta\eta\xi}). \quad (12)$$

All interaction-induced properties were calculated at the CCSD level using the DALTON program package [24], whose implementation is described in [21–23, 25, 26].

Our previous experience [2–5] indicates that the d-aug-cc-pVQZ-33211 basis set is adequate [27–29], in terms of accuracy and cost effectiveness, to evaluate these properties, and it is employed in the calculations of the heteronuclear dimers. In order to further check its adequacy, for the He–Ar dimer we performed calculations at $R=6.0$ au with the d-aug-cc-pVXZ-33211 (X = T, Q, 5), sequence of bases. The results confirmed the efficiency of the d-aug-cc-pVQZ-33211 basis set. We expect the frequency dependence of the properties to make a small contribution to the overall property, as observed in previous studies for the homonuclear dimers [2, 3]. Therefore, we only tested the static contributions for basis set demands.

The rovibrational analysis and the determination of the gas virial coefficients were carried out using KORG [30].

3. Results and Discussion

3.1 *Interaction-induced potential energy*

The results obtained for the interaction energies are presented in table 1 and the analytical functions to which they are fitted in table 2. The internuclear potentials have been determined by several authors. The most accurate results in the literature are those by Cybulski and Toczylowski [6], who employed CCSD(T) and the aug-cc-pV5Z basis set supplemented with $3s3p2d2f1g$ midbond functions. The work of Cybulski and Toczylowski was very recently extended by Giese and co-workers [7], who performed calculations, using the same basis set and the same method, for a wide range of internuclear distances and determined second virial coefficients and Boyle temperatures. Internuclear potentials for He–Ar and He–Ne were also obtained by Petsalakis *et al.* [13] using the multireference configuration interaction method. These results are anyhow less accurate than those of [6]. The potentials obtained by Cybulski and Toczylowski [6] are very similar to the present CCSD(T)/aug-cc-pV6Z-33211 potentials. These authors concluded, based on the comparison of their frequencies of vibrational and rotational transitions with the accurate experimental data available for the Ne_2 [31], Ar_2 [32, 33] and Ne–Ar complexes [8], that their theoretical potentials were a bit too shallow. This in spite of the fact that the computed *ab initio* dissociation energies of the He–Ne and He–Ar dimers were larger than those available from empirical potentials for the He–Ar and the He–Ne complexes [34]. Cybulski and Toczylowski concluded that these empirical potentials underestimate the well depths for these two complexes.

Table 2. Parameters of the fit for the ground state potentials of the He–Ar, Ne–Ar and He–Ne mixed dimers calculated at the CCSD(T)/aug-cc-pV6Z-33211 level. The fitting function is in all cases that proposed by Korona et al. [44]: $V(R)=Ae^{-aR+\beta R^2}-\sum_{n=3}^{8}f_{2n}(R,b)c_{2n}/R^{2n}$, with $f_{2n}(R,b)=1-e^{-bR}-\sum_{k=0}^{2n}(bR)^k/k!$. Atomic units are used unless specified otherwise. The resulting energies are in μE_h.

	He–Ne	He–Ar	Ne–Ar
A	24.39281476	23.03058634	75.46127492
α	2.06719912	1.63051044	1.74950215
β	−0.03101869	−0.04680016	−0.03696981
b	2.59345555	1.62747925	1.62629958
c_6	3.06231479	9.40835513	19.00663350
$c_8\times10^{-2}$	0.31679810	1.65523018	3.92862647
$c_{10}\times10^{-3}$	0.42773150	3.79715796	10.56270065
$c_{12}\times10^{-4}$	0.77251599	11.65179999	37.98789997
$c_{14}\times10^{-6}$	0.18194500	4.66258000	17.81600000
$c_{16}\times10^{-8}$	0.05440120	2.36861000	10.60750000

Good agreement with the estimates of Ogilvie and Wang [34] was found for the rotational energy levels (of the ground vibrational state) supported by Cybulski and Toczylowski's potentials, although e.g. the second vibrational level predicted for the He–Ar dimer could not be obtained in the *ab initio* study, in spite of the larger dissociation energy, that is depth of the well [6].

The present results from the rovibrational analysis are given in table 3. From our potentials we can determine equilibrium dissociation energies D_e of 66.62, 94.24 and 205.93 μE_h for the He–Ne, He–Ar and Ne–Ar dimers,

Table 3. Rovibrational analysis of the potential curves, calculated at the CCSD(T)/aug-cc-pV6Z-33211 level, for the He–Ne, He–Ar and Ne–Ar mixed dimers. R_e is the equilibrium distance of the ground vibrational state ($\upsilon = J = 0$), where the potential curve has its minimum, $V(R_e)$, corresponding to the dissociation energy, D_e. R_{ave} is the average internuclear distance for the ground vibrational state. D_n is the dissociation energy with respect to the vibrational state $\upsilon = n$, $J = 0$ (the corresponding average internuclear distances for $n > 0$ are given in square brackets). $\upsilon' - \upsilon''$ are the energy differences between vibrational levels (transition frequencies). $J' - J''$ are the energy differences between rotational levels of the ground vibrational state ($\upsilon = 0$).

	He–Ne[a]		He–Ar[b]		Ne–Ar[c]	
	This work	Ref. [6]	This work	Ref. [6]	This work	Ref. [6]
Re/bohr	5.723	5.7224	6.599	6.5998	6.601	6.6015
$De/(\mu E_h)$	66.6166	66.67	94.2441	94.15	205.9275	205.87
R_{ave}/bohr	7.5165	7.5195	7.6996	7.7014	6.8881	6.8889
D_0/cm^{-1}	2.5812	2.5700	7.0318	7.0144	32.4818	32.4713
D_1/cm^{-1}	0.0001		0.0005		14.0285	
	[34.2250]		[34.6882]		[7.6997]	
D_2/cm^{-1}					4.0142	
					[9.2198]	
D_3/cm^{-1}					0.4136	
					[13.2500]	
D_4/cm^{-1}					0.0006	
					[40.2281]	
B_0/cm^{-1}		0.3599	0.2957	0.2957	0.0965	0.09647
$\upsilon' - \upsilon''/cm^{-1}$	This work	Ref. [6]	This work[d]	Ref. [6]	This work[d]	Ref. [6]
$1 - 0$	2.5811	—	7.0313	—	18.4533	18.45
			[5.76 ± 0.32]		[19.103 ± 0.010]	
$2 - 1$					10.0143	10.01
					[10.272 ± 0.058]	
$3 - 2$					3.6006	3.60
					[2.44 ± 0.22]	
$4 - 3$					0.4130	—
$J' - J''/cm^{-1}$	This work	Ref. [6][d]	This work	Ref. [6][d]	This work	Ref. [6][e, f]
$1 - 0$	0.7095	0.7092	0.5896	0.5895	0.1929	0.1929
		[0.706 ± 0.033]		[0.5897 ± 0.0085]		[0.1944]
$2 - 1$	1.3398	1.3387	1.1673	1.1671	0.3858	0.3856
		[1.348 ± 0.039]		[1.1670 ± 0.0093]		[0.3887]
$3 - 2$			1.7184	1.7180	0.5781	0.5780
				[1.717 ± 0.011]		[0.5826]
$4 - 3$			2.2180	2.2172	0.7700	0.7698
						[0.7759]

[a] Empirical potential results: $R_e = 5.7362$ bohr; $D_e = 66.16\,\mu E_h$, Ref. [45]; $R_e = 5.7276$ bohr; $D_e = 65.53\,\mu E_h$, Ref. [34].
[b] Empirical potential results: $R_e = 6.5718$ bohr; $D_e = 93.89\,\mu E_h$, Ref. [45]; $R_e = 6.5770$ bohr; $D_e = 91.60\,\mu E_h$, Ref. [34].
[c] Rotational spectroscopy results: $R_e = 6.5453$ bohr; $D_0 = 32.890\,cm^{-1}$; $B_0 = 0.09723\,cm^{-1}$, Ref. [8]. Empirical potential results: $R_e = 6.5931$ bohr; $D_e = 214.04\,\mu E_h$, Ref. [34].
[d] Values within brackets from the empirical potential in Ref. [34].
[e] Values within brackets from the experimental results in Ref. [8].
[f] See also 0.194 05 ± 0.000 49 (1 − 0), 0.387 92 ± 0.000 49 (2 − 1), 0.581 33 ± 0.000 53 (3 − 2), Ref. [34].

respectively. The equilibrium geometries (R_e) are 5.723, 6.599 and 6.601 bohr, respectively.

When comparing the present results with the accurate experimental data available for the Ne–Ar complex [8] we can see that the dissociation energy and equilibrium distance improve slightly upon Cybulski and Toczylowski's results [6]. Still the dissociation energy is underestimated. In general, for the three mixed dimers the results are very close to those of [6], and still consistently closer to those of the empirical potentials.

The CCSD(T)/aug-cc-pV6Z-33211 potentials support two bound vibrational levels each for He–Ne and He–Ar and five for Ne–Ar; in all cases one state more than the potentials from [6] in spite of the fact that the potentials are very close to each other. Ogilvie and Wang's potentials [34] yield two states for He–Ar, but only one for He–Ne and three for Ne–Ar. However, the highest excited vibrational levels predicted by the present potentials are close to the dissociation limit ($< 0.01\,\mathrm{cm}^{-1}$). In table 3 we report also the average internuclear distance of each vibrational state. The higher vibration levels are as expected quite delocalized, with the maximum radial distribution ranging from about 34–35 bohr for the He–Ne and He–Ar dimers to about 40 bohr for the Ne–Ar system.

The first three transition frequencies, $(\upsilon' - \upsilon'') = (D_n - D_{n-1})$, of the Ne–Ar dimer practically coincide with those of [6]. We thus agree with Cybulski and Toczylowski's conclusion regarding the incorrect value of the 3−2 transition frequency calculated by Ogilvie and Wang [34].

The energy differences between rotational levels of the ground vibrational state, $J' - J''$, are also reported in table 3. For the Ne–Ar complex they are in all cases closer to the accurate experimental results than Cybulski and Toczylowski's results are. For the He–Ne and the He–Ar complexes our results are always slightly larger than those given in [6], and they disagree with those evaluated in [34].

A test for the quality of the potential curves is given by the evaluation of the gas virial coefficients which, if quantum effects are neglected, are obtained by the semiclassical integral

$$B(T) = -2\pi N_A \int_0^\infty \left[\exp\left(-V(R)/kT\right) - 1\right] R^2 dR, \quad (13)$$

where N_A is Avogadro's number, k indicates Boltzmann's constant and T is the temperature.

The results obtained with the CCSD(T)/aug-cc-pV6Z-33211 potentials are plotted in figure 1, where we compare with the available experimental data (see also [35]). Gas virial coefficients of the mixed dimers of helium, neon and argon were also computed by Giese and co-workers [7] at a semiclassical level with perturbative quantum corrections, starting essentially from the potential of [7]. In the present study the semiclassical integration is carried out in the 0.05 to 500.0 bohr range. Convergence in the semiclassical integral was checked by extending the integration range to shorter and larger R values.

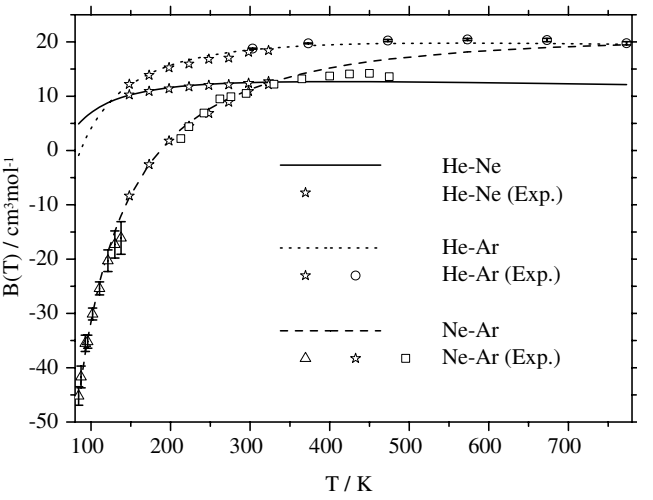


Figure 1. Temperature dependence of the He–Ne, He–Ar and Ne–Ar gas second virial coefficients, $B(T)$. Comparison is made with previously available experimental results: stars, Ref. [36]; circles, Ref. [37]; squares, Ref. [38]; triangles, Ref. [39].

Agreement with experiment is reasonably good, in particular for the He–Ne dimer. Differences rising up to about $1\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ appear, however, between the *ab initio* results and Brewer and Vaughn [36] observations for the He–Ar dimer at and below room temperature, with calculations predicting higher values. Theory falls on the other hand below the Kalfoglou and Mille [37] measurements, often outside their error bars, at higher temperatures. None of the temperatures for these measurements is so low as to lead to suspect quantum effects for the disagreement between experiment and the calculated values. Our previous analyses of the interaction properties of the homonuclear rare gas complexes have indeed shown that quantum effects are completely negligible at the temperatures of Brewer and Vaughn's measurements. For the He–Ne mixed dimer, in the same temperature range, good agreement between the present *ab initio* results and the experimental data of [36] is observed. Schmiedel *et al.*'s [38] measurements for the virial coefficient of the Ne–Ar complex do not show on the other hand a smooth behaviour with temperature, and theory diverges from these numbers as the temperature increases. At temperatures below 100 K, down to about 80 K, still most likely far from the range where quantum effects

become important, the theoretical semiclassical results remain within the error bars of Shamma and Rigby's measurements [39].

3.2. *Interaction-induced electric properties*

A summary of the results for the interaction-induced dipole moments is presented in table 4 whereas the interaction (hyper)polarizabilities and the corresponding dispersion coefficients can be found in tables 5 and 6. All these values were fitted to analytic functions whose forms together with the parameters of the fits and the complete set of results for the properties can be obtained from the authors on request. In figures 2 to 5 the (static part of the) properties for the three dimers are plotted together with the fitting functions. The Ne–Ar results for $\Delta\mu$, $\Delta\alpha_{ave}$, $\Delta\alpha_{ani}$ and $\Delta\beta_{||}$ are also compared to those evaluated by Maroulis and Haskopoulos [11].

The properties of the mixed dimers are similar to those of the corresponding homonuclear dimers [2–5]. On the other hand, the lowest-order dispersion contributions to the properties do not always parallel the behaviour of the corresponding static properties, opposite to what happens for the homonuclear dimers [2–5]. The functional forms needed to fit the calculated properties were in many cases different from those employed for the corresponding dispersion coefficients. Both $\Delta\alpha_{ave}$ and $\Delta S_{ave}(-4)$ are negative for short internuclear distances, reach a maximum and then decrease to zero. $\Delta\alpha_{ani}$ and $\Delta S_{ani}(-4)$ are positive over the whole range of internuclear distances, with the exception of $\Delta S_{ani}(-4)$ for the He–Ar complex, which displays a negative minimum and then increases to a positive maximum before going asymptotically to zero. $\Delta\beta_{||}$, $\Delta(\beta_{||}\times A)$ and $\Delta\beta_K(2)$ are negative at short internuclear distances, reach a maximum and decrease to zero. Finally, $\Delta\gamma_{||}$, $\Delta(\gamma_{||}\times A)$ and $\Delta D_K(2)$ display a negative minimum at small distances, increase to a positive maximum and then decrease monotonically to zero.

The only references in the literature to *ab initio* studies of the interaction-induced electric properties of the mixed rare gas dimers, in particular interaction-induced (hyper)polarizabilities, are, to our knowledge, due to the work of Maroulis and co-workers [10,11]. Maroulis first [10], and then Maroulis and Haskopoulos [11] considered, among other complexes, the Ne_2, Ne–Ar, Ne–HF and Ne–FH mixed dimers using different methods and basis sets. Some of the limitations of their analysis were discussed already in [4] with reference to the neon dimer. In [11] these authors presented results for the induced dipole moment and induced static polarizability of Ne–Ar obtained at the self-consistent field (SCF) and CCSD(T) level using a [7*s*5*p*4*d*1*f*/8*s*6*p*5*d*3*f*] basis set and at the SCF and B3LYP level using a [7*s*5*p*5*d*3*f*/8*s*6*p*5*d*4*f*] basis set. Results for the static first hyperpolarizabilities were obtained in the first basis set at the SCF, MP2, CCSD and CCSD(T) level, and at the SCF, MP2 and B3LYP level using the second basis set. The authors concluded that even density functional theory might be used to obtain reasonable estimates of the properties.

The results of [11] are in all cases lower than the values obtained in the present study for $\Delta\mu$ and $\Delta\alpha_{ave}$ (by ≈10–15% in the worst case), with differences that become larger as the interatomic distance decreases (see figures 2 to 3). For $\Delta\alpha_{ani}$ their results are always larger than ours, still with differences increasing at shorter interatomic distances, see figure 4. Note, however, that only four decimal digits for $\Delta\mu$ and two for $\Delta\alpha_{ani}$ are given in the tables of [11].

Since the results of Maroulis and Haskopoulos are CCSD(T) whereas ours are obtained by exploiting a CCSD approach, the existing discrepancies might be due to a deficiency of the correlation treatment at the

Table 4. CCSD/d-aug-cc-pVQZ-33211 results for the interaction-induced dipole moments $\Delta\mu$. Atomic units are used.

R	He–Ne	R	He–Ar	R	Ne–Ar
3.5	4.63822×10^{-3}	3.0	-1.5257755×10^{-1}	4.5	-5.845717×10^{-2}
4.0	5.1452×10^{-4}	4.0	-5.310786×10^{-2}	5.0	-2.719408×10^{-2}
5.0	-2.7399×10^{-4}	5.0	-1.457776×10^{-2}	6.0	-5.09856×10^{-3}
6.0	-7.410×10^{-5}	6.0	-3.02892×10^{-3}	7.0	-6.6608×10^{-4}
7.0	-1.274×10^{-5}	7.0	-4.4467×10^{-4}	8.0	1.939×10^{-5}
8.0	-1.99×10^{-6}	8.0	-9.84×10^{-6}	9.0	6.676×10^{-5}
9.0	-5.2×10^{-7}	9.0	3.109×10^{-5}	10.0	3.979×10^{-5}
10.0	-1.0×10^{-7}	12.0	3.97×10^{-6}	12.0	7.54×10^{-6}
12.0	2.2×10^{-7}	14.0	1.24×10^{-6}	14.0	1.63×10^{-6}
14.0	1.3×10^{-7}	16.0	5.5×10^{-7}	16.0	9.1×10^{-7}
16.0	2×10^{-8}	18.0	2.6×10^{-7}	18.0	5.1×10^{-7}
18.0	-1×10^{-8}	20.0	1.2×10^{-7}	20.0	2.5×10^{-7}

Table 5. CCSD/d-aug-cc-pVQZ-33211 interaction-induced polarizabilities $\Delta\alpha_{ave}$ and $\Delta\alpha_{ani}$, and first hyperpolarizability $\Delta\beta_{\|}$. Also, Cauchy moments $\Delta S_{ave}(-4)$ and $\Delta S_{ani}(-4)$, and first $\Delta(\beta_{\|} \times A)$, $\Delta\beta_K(2)$ hyperpolarizability dispersion coefficients. All quantities are given in atomic units.

R	$\Delta\alpha_{ave}$	$\Delta S_{ave}(-4)$	$\Delta\alpha_{ani}$	$\Delta S_{ani}(-4)$	$\Delta\beta_{\|}$	$\Delta(\beta_{\|} \times A)$	$\Delta\beta_K(2)$
				He–Ne			
3.50	−0.114004	−0.310725	0.180882	0.177588	−0.290358	−1.793806	−3.309275
4.00	−0.062055	−0.207398	0.170032	0.179511	−0.336436	−1.539265	−2.893940
6.00	−0.000933	−0.009916	0.094055	0.184205	−0.053439	−0.256830	−0.508291
8.00	0.000342	0.000982	0.041963	0.092148	−0.001252	−0.012154	−0.025088
10.00	0.000099	0.000380	0.021441	0.047379	0.000509	0.001242	0.002319
12.00	0.000036	0.000137	0.012389	0.027332	0.000236	0.000688	0.001330
14.00	0.000015	0.000058	0.007794	0.017177	0.000075	0.000261	0.000499
16.00	0.000006	0.000023	0.005216	0.011486	0.000018	0.000077	0.000140
18.00	0.000002	0.000009	0.003661	0.008057	0.000001	0.000005	0.000003
				He–Ar			
4.00	−0.267978	−1.396301	0.431255	−0.534027	−10.629428	−53.848584	−107.690514
6.00	−0.027720	−0.310994	0.320743	0.544090	−2.433407	−15.914910	−32.119283
8.00	0.001202	−0.008890	0.173049	0.578294	−0.185590	−1.803854	−3.671196
10.00	0.000792	0.004649	0.090189	0.328155	0.003224	−0.046882	−0.099350
12.00	0.000267	0.001894	0.051992	0.189838	0.004064	0.025623	0.050445
14.00	0.000103	0.000738	0.032661	0.118946	0.001300	0.010487	0.020643
16.00	0.000046	0.000326	0.021853	0.079458	0.000536	0.004037	0.007950
18.00	0.000023	0.000159	0.015337	0.055715	0.000294	0.001737	0.003442
20.00	0.000012	0.000080	0.011175	0.040571	0.000141	0.000721	0.001436
				Ne–Ar			
4.50	−0.270470	−1.297338	0.767303	0.793946	−10.517364	−46.868623	−93.542757
6.00	−0.040368	−0.390170	0.630449	1.469468	−3.117411	−18.039893	−36.197817
8.00	0.003469	0.001220	0.333570	1.138284	−0.228740	−2.031888	−4.114677
10.00	0.001696	0.010796	0.172911	0.624559	0.010308	0.007379	0.008883
12.00	0.000593	0.004128	0.099588	0.359603	0.006279	0.049163	0.097061
14.00	0.000239	0.001620	0.062526	0.225042	0.001886	0.017845	0.035355
16.00	0.000100	0.000681	0.041809	0.150194	0.000907	0.007045	0.014004
18.00	0.000047	0.000316	0.029332	0.105259	0.000568	0.003312	0.006640
20.00	0.000024	0.000159	0.021370	0.076638	0.000289	0.001497	0.003011

CCSD level. On the other hand, the accuracy we achieved in our previous determinations of these properties for the homonuclear complexes [2–5] would lead us to believe that the differences are mainly due to the different basis sets used here and in [11].

For the interaction polarizabilities Maroulis and Haskopoulos reproduce the qualitative behaviour of the property curve obtained here. However, the distance dependence of $\Delta\beta_{||}$ as described by the CCSD or CCSD(T) results in [11] is not entirely in qualitative agreement with the present results (see figure 5), in particular around 7 au. This gives further indication of the limitedness of the basis set used in [11] for evaluating these properties. $\Delta\beta_{||}$ is also apparently the case where, in our opinion, the B3LYP approach can achieve only a limited accuracy (see figure 5). In the region between 7 and 10 bohr the values oscillate, change in sign, and deviate remarkably from our fit.

It is of interest to compare the behaviour of the properties of heteronuclear dimers (both static part and frequency dispersion coefficients) with those of the homonuclear van der Waals complexes, see [2–5]. For the Ne–Ar complex the properties of the mixture assume in general values intermediate between those of the Ar and the Ne gases. For $\Delta\gamma_{||}$ the dispersion coefficients are lower than those of the pure gases at small internuclear distances, but they get larger at long internuclear distances. For $\Delta S_{ani}(-4)$ the mixed dimer always has a higher value than that of the homonuclear complexes. In the case of the He–Ne complex both for $\Delta\alpha_{ave}$ and $\Delta\gamma_{||}$ and for their dispersion coefficients the properties of the mixed dimer lie in between those of the homonuclear dimers, whereas in the case of $\Delta\alpha_{ani}$ they are lower than those of either He_2 or Ne_2. For the polarizability, the behaviour of the mixed dimers is markedly determined by that of Ne. In the He–Ar

Table 6. CCSD/d-aug-cc-pVQZ-33211 interaction-induced second $\Delta\gamma_{\|}$ hyperpolarizability and second $\Delta(\gamma_{\|} \times A)$, $\Delta D_K(2)$ hyperpolarizability dispersion coefficients. All quantities are given in atomic units.

R	$\Delta\gamma_{\|}$	$\Delta(\gamma_{\|} \times A)$	$\Delta D_K(2)$
		He–Ne	
3.50	−10.9609	−29.4168	−57.0304
5.00	−4.9080	−19.8202	−40.7094
8.00	0.0406	−0.1446	−0.3354
10.00	0.0420	0.1385	0.2660
12.00	0.0173	0.0630	0.1207
14.00	0.0076	0.0269	0.0517
16.00	0.0031	0.0109	0.0213
18.00	0.0011	0.0041	0.0080
		He–Ar	
4.00	−61.8779	−381.8507	−708.1409
6.00	−38.8821	−331.2336	−667.6760
8.00	−4.1478	−52.5003	−107.7921
10.00	0.2396	−1.3608	−3.2466
12.00	0.2338	1.5379	2.9104
14.00	0.1021	0.7654	1.4470
16.00	0.0456	0.3412	0.6393
18.00	0.0211	0.1579	0.2967
20.00	0.0097	0.0740	0.1422
		Ne–Ar	
4.50	−50.4116	−197.3860	−366.0600
6.00	−40.8273	−309.0031	−623.4293
8.00	−3.4017	−47.1737	−98.0709
10.00	1.0098	3.5381	6.1216
12.00	0.5610	3.7331	7.1047
14.00	0.2376	1.6739	3.1622
16.00	0.0999	0.7180	1.3470
18.00	0.0440	0.3218	0.6077
20.00	0.0200	0.1491	0.2878

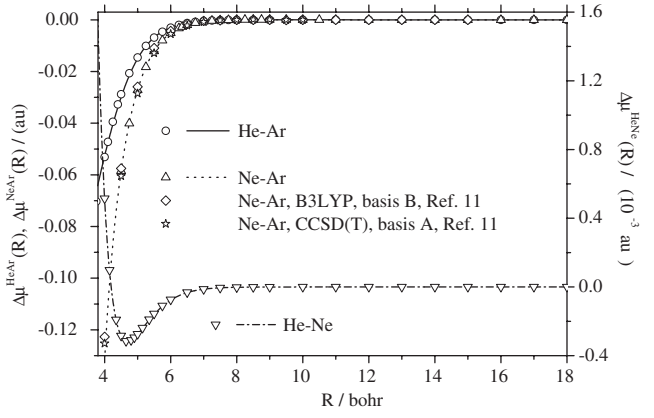


Figure 2. Interaction-induced dipole moments $\Delta\mu(R)$ of the He–Ne, He–Ar and Ne–Ar mixed dimers as a function of the interatomic distance R, and the analytical functions fitted to them (see text). The B3LYP and CCSD(T) results of Maroulis and Haskopoulos for the Ne–Ar dimer (see [11]) are also shown.

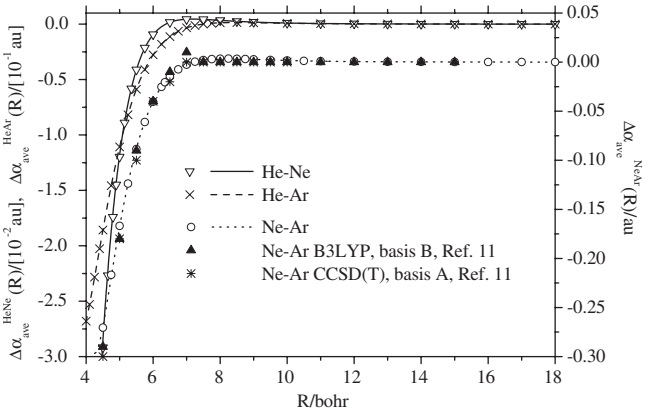


Figure 3. Interaction-induced static isotropic polarizabilities $\Delta\alpha_{ave}(R)$ of the He–Ne, He–Ar and Ne–Ar mixed dimers as a function of the interatomic distance R, and the analytical functions fitted to them (see text). The B3LYP and CCSD(T) results of Maroulis and Haskopoulos for the Ne–Ar dimer (see [11]) are also shown.

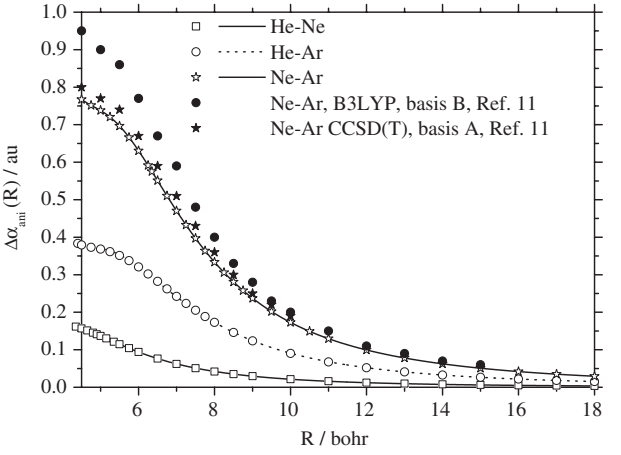


Figure 4. Interaction-induced static anisotropic polarizabilities $\Delta\alpha_{ani}(R)$ of He–Ne, He–Ar and Ne–Ar mixed dimers as a function of the interatomic distance R, and the analytical functions fitted to them (see text). The B3LYP and CCSD(T) results of Maroulis and Haskopoulos for the Ne–Ar dimer (see [11]) are also shown.

complex the trends are more variable and it is difficult to recognize a general behaviour, although it is fair to say that the greater influence on the properties of the mixture comes in general from the Ar atom.

4. Summary and Conclusions

The interaction-induced potential, electric dipole moment, polarizabilitiy and first and second hyperpolarizability of the He–Ne, He–Ar and Ne–Ar van der Waals complexes have been evaluated, as a part of an ongoing project involving the study of the effect of two-body interactions on the properties of rare gases.

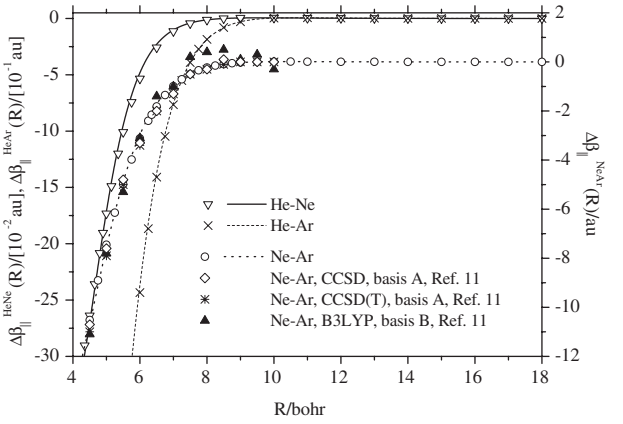


Figure 5. Interaction-induced static mean first hyperpolarizabilities $\Delta\beta_{\|}(R)$ of He–Ne, He–Ar and Ne–Ar mixed dimers as a function of the interatomic distance R, and the analytical functions fitted to them (see text). The B3LYP, CCSD and CCSD(T) results of Maroulis and Haskopoulos for the Ne–Ar dimer (see [11]) are also shown.

Within this framework we have determined in recent times interaction-induced electric dipole polarizabilities and second hyperpolarizabilities of helium, neon and argon [2–5], interaction-induced magnetizability and mixed electric/magnetic hypermagnetizability [40], chemical shielding [41], quadrupole moment and higher mixed electric dipole/electric quadrupole/magnetic dipole hyperpolarizabilities [42] of helium. These quantities, among others, have been employed to analyse the density dependence of the Kerr birefringence of helium, neon and argon [2, 4, 43], of the Cotton—Mouton (magnetic induction field induced) [40] and Buckingham (electric field gradient induced) [42] birefringences and of the chemical shielding [41] of helium.

For the calculation of the potential we employ the aug-cc-pV6Z-33211 basis set and the coupled cluster singles and doubles (CCSD) model corrected for the triple excitations — CCSD(T). For the electric properties the d-aug-cc-pVQZ-33211 basis set and CCSD response theory were employed. The rovibrational spectra and gas second virial coefficients were computed, in order to check the quality of the potential curve. The rovibrational spectra slightly improve over the previously available theoretical results, giving excellent agreement for properties such as the vibrational and rotational energy differences and for the equilibrium distances, but still probably underestimating the dissociation energies. For the virial coefficients the agreement with the available experimental data can be considered fairly accurate, even at temperatures as low as 80 K.

The results for the interaction-induced electric dipole moments and static (hyper)polarizabilities show the usual behaviour in terms of the dependence on the internuclear distance. Also, the frequency dependence of the properties is in the order of magnitude expected on the basis of our previous results for the homonuclear dimers [2–5].

The data discussed above are used in an ongoing work to determine the virial coefficients of various optical phenomena associated with the electrical properties [14].

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