Theoretical study on the complexes of He, Ne and Ar*

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This paper investigates the effect of basis sets through the potential energy curves (PECs) of six rare gas complexes He_2, Ne_2, Ar_2, He–Ne, He–Ar, and Ne–Ar. The coupled cluster singles and doubles method with perturbative treatment of triple excitations, doubly augmented basis sets of d-aug-cc-pVQZ, bond functions, and basis set superposition errors are employed. The diffuse function is more effective than the polarization function on describing the dissociation energy. The PECs are fitted into analytical potential energy functions (APEFs) using three expressions. It is found that all the expressions are suitable for describing the complexes of rare gases. Based on these APEFs, the spectroscopic parameters are calculated and the results are compared with the theoretical and experimental data available in the literature.

Keywords: potential energy curve, analytical potential energy function, spectroscopic parameter

PACC: 3150, 3420, 3180

1. Introduction

The van der Waals complexes are bound with weak interactions, and they play a critical role in understanding the process that the molecules and atoms solvate in the nanoscale droplets.[1,2] In particular, the rare gas complexes, as the family of species that represent the typical characters of van der Waals system, have been explored by many researchers recently.[3−6] Moreover, as the development of the technology, it has aroused much attention to employ the rare gas atoms to produce the ultracold environment in experiment. The rare gas atom He and Ne have already been experimentally used as buffer-gas to trap Cu and Ag.[7,8]

In fact, researchers have given much concern on the complexes of rare gases. Experimentally, for the Ar_2 complex, in 1976, Colbourn *et al.*[9] obtained the absorption spectrum of Ar_2. Then Tanaka *et al.*[10] and Frenkel *et al.*[11] gave the emission and Raman spectrum, respectively. Dehmer[12] and Herman *et al.*[13] reported the photo-ionization of Ar_2 at high resolution and the constants of the ground and excited states. For the He–Ne and He–Ar, Keil *et al.*[14] used high-resolution differential cross sections and accurate new limiting diffusion measurements to obtain their interatomic potentials. For the Ne_2 complex, Wüest *et al.*[15] determined the interaction potential of the ground electronic state of Ne_2 by high-resolution vacuum ultraviolet laser spectroscopy in 2003. For the Ne–Ar complex, the rotational constants, the microwave transition frequencies and so on have been reported by Grabow *et al.*[16] At the same time, there are theoretical investigations for these systems. In 2001, Tatiana used the symmetry-adapted perturbation theory method to calculate the potential energy curves (PECs) of He_2.[17] Partridge *et al.*[18] studied the PECs of He–Ne and He–Ar by using the basis set of aug-cc-pVQZ with the bond functions of 3s3p2d1f1g.[19] Fernández *et al.*[20] reported the ground state $X^1\Sigma_g^+$ and the excited state $B^1\Sigma_u^+$ of Ar_2 using different coupled cluster (CC) method and Slavíček employed the aug-cc-pVXZ (X=D, T, Q, 5, 6) basis set added three different bound functions[19] to compute the PEC of Ar_2.[21] Hättig[22] reported the frequency-dependent interaction induced polarizabilities of He_2 and improved the calculations of the static interaction induced polarizabilities of Ar_2. In 1999, Cybulski *et al.*[23] systematically obtained the PECs for these six complexes of rare gases. However, their results still had some difference in comparison with the experimental ones.

The analytical potential energy function (APEF) is the effective and convenient expression for studying the transport properties and understanding the intermolecular forces and dynamics. Many researchers are inclined to use the Tang–Toennies (TT) potential[15,23−26] to represent the energy curves of the rare gas complexes, except Keil *et al.*[14] and Aziz *et*

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al.[27] employed the Hartree–Fock plus damped dispersion potential form. Considering that the Murrell–Sorbie[28−38] (MS) function is usually used to fit common bound states of diatomic molecules and Huxley (HUX)[39] function is usually employed to describe the weak interactions, we try to fit the calculated PECs into the expressions of TT, MS and HUX.

In this paper, the PECs with high accuracy for the rare gas complexes have been obtained through elaborate calculations with the emphasized effect of basis sets. The PECs are fitted into APEFs using three expressions. The spectroscopic parameters are determined based on the APEFs.

2. Computational details

All the calculations for the PECs of rare gas complexes are performed by using the MOLPRO package[40] running on the Dawning-4000A computer[41] at Ludong University. The PECs are fitted into the three APEFs by using the non-linear least square fitting method. According to the work of Woon *et al.*[42] CC singles and doubles including connected tripled corrections [CCSD(T)] can give better results than that of the fourth-order many-body perturbation theory (MP4) for the complex of Ar_2. Fernández *et al.*[20] confirmed that the CCSD method with the addition of the triples correction is one of the most powerful methods for the evaluation of molecular properties of the ground state of Ar_2. More investigations[3,18,21−23] show that the single configuration method can well describe the interaction in van der Waals complexes. So the CCSD(T) method is employed to investigate the ground states of rare gas complexes in this work.

As is well known, the calculations of the weak bound complexes are sensitive to the basis sets. The polarization functions and the diffusion functions are two kinds of functions to improve the quality of basis sets. Generally, the polarization functions can describe the polarization effect which distorts the shape of the atomic orbitals. The diffuse functions can be more effective to represent the "tail" portion of the atomic orbitals. For these complexes with very weak interactions, the "tail" becomes much more important because the interaction spans long distance of the atomic nuclei. Therefore, in this work, the diffuse functions are added in the augmented correlation consistent sets for the rare gas atoms. The doubly augmented basis sets d-aug-cc-pVQZ are used to describe the interaction. For rare gases He and Ne, the d-aug-cc-pVQZ basis sets, i.e., (7s, 3p, 2d, 1f) → [4s, 3p, 2d, 1f] plus 1s1p1d1f plus 1s1p1d1f for He and (12s, 6p, 3d, 2f, 1g) → [5s, 4p, 3d, 2f, 1g] plus 1s1p1d1f1g plus 1s1p1d1f1g for Ne, are used. While for Ar atom, no explicit d-aug-cc-pVQZ basis sets are available. Based on the principle of obtaining the exponents for the additional functions reported by Woon *et al.*,[43] we produced one. The additional exponents in the d-aug-cc-pVQZ sets can be written as: s/0.02171, p/0.01523, d/0.04327, f/0.15917, g/0.20921, respectively. In addition, the bond functions play an important role in the weak complexes and it is not negligible for the rare gas complexes, a set of 3s3p2d2f1g[19] bond functions is employed in the present work. The counterpoise procedure of Boys and Bernardi is used to circumvent the basis set superposition error (BSSE).[44]

3. The analytical potential energy functions

In order to exploring the suitable form of APEF to well represent the weak interactions for the rare gas complexes, we use three expressions to fit the PECs and determine the spectroscopic parameters.

3.1. The TT potential model

Tang and Toennies suggested that the TT potential can well represent the van der Waals complexes[25] but is not suitable for the common molecules with very deep well such as CaF.[31] The TT potential which was used by Korona *et al.*[45] can be written as

$$V(R) = A\exp(-\alpha R+\beta R^2) - \sum_{n=3}^{8}\left[1-\exp(-bR)\left(\sum_{K=0}^{2n}\frac{(bR)^K}{K!}\right)\right]\frac{C_{2n}}{R_{2n}}. \quad (1)$$

In this model, R represents the internuclear distance and C_{2n} denote the dispersion coefficients. For many systems, the formula may be terminated at $n_{\max}=5$. Then the analytical potential is determined by only seven parameters A, α, β, b, C_6, C_8, and C_{10}. However, for the complexes of rare gas, higher dispersion coefficients are needed to accurately describe the weak interaction. The higher dispersion coefficients are derived from the extrapolation formulas of Thakkar *et al.*[46]

$$C_{2n+4} = \frac{\Omega_n C_{2n-2}}{(C_{2n}/C_{2n+2})^3}, \quad (2)$$

$$\Omega_n = \frac{(2n+1)(2n+3)n^3(n-2)(2^n-1)(2^{n-2}-1)^3}{(2n-1)^2(n+1)(n-1)^3(2^{n-3}-1)(2^{n-1}-1)}. \quad (3)$$

Usually, some researchers denoted $\Omega_n \approx 1$. In order to obtain more accurate coefficients for these complexes of rare gases, according to Eqs. (2) and (3), we determined $C_{12} = 1.0286C_6(C_{10}/C_8)^3$, $C_{14} = 0.9749C_8(C_{12}/C_{10})^3$ and $C_{16} = 0.9735C_{10}(C_{14}/C_{12})^3$, respectively. The C_6, C_8 or C_{10} is unphysical when they are negative, so the parameters b, C_6, C_8 and C_{10} are fixed firstly corresponding to the data existed availably,[23,47–50] and the A, α, and β are treated as adjustable parameters. Then all the ten parameters participate in the fitting work.

3.2. The MS function

The MS function[28] is regarded as one of the best APEFs to describe the most diatomic molecules or ions.[28–36] Generally, MS function is used to describe the PECs of deep well. However, it can also give good results for weak interactions if the polynomials are terminated at higher order.[51] The MS form used in the present work is as follows:

$$\begin{aligned} V(\rho) = & -D_e(1 + a_1\rho + a_2\rho^2 + a_2\rho^2 \\ & + a_3\rho^3 + a_4\rho^4 + a_5\rho^5 + a_6\rho^6 \\ & + a_7\rho^7 + a_8\rho^8 + a_9\rho^9)\exp(-a_1\rho). \end{aligned} \quad (4)$$

In this formula, $\rho = R - R_e$, where R represents the internuclear distance, R_e is the equilibrium distance, and D_e is the dissociation energy. In the fitting process there are eleven parameters including the R_e and D_e.

3.3. The HUX function

The HUX function[39] can well represent the long range potential of the van der Waals system, this function is

$$\begin{aligned} V(R) = & A(1 + a_1R + a_2R^2 + a_3R^3)\exp(-a_4R) \\ & + \tanh(R - R_m/2) \\ & \times (C_6R^{-6} + C_8R^{-8} + C_{10}R^{-10}). \end{aligned} \quad (5)$$

The three parameters C_6, C_8 and C_{10} are the dispersion coefficients which describe the long range interactions, respectively. R_e and R represent the equilibrium and internuclear distance. In the present work, all the nine parameters are fitted from the calculated PECs.

In order to judge the quality of the fitting results and the suitability of the three expressions of APEFs, we calculate the root mean square (RMS) error. It can be represented by the formula[36]

$$\mathrm{RMS} = \sqrt{\frac{1}{M}\sum_{i=1}^{M}(V_{\mathrm{MS}}(i) - V_{ab-initio}(i))^2}. \quad (6)$$

4. The spectroscopic parameters

Based on the APEFs obtained from the functions described above, the spectroscopic parameters are calculated by the following equations:

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad (7)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \quad (8)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{f_3R_e}{3f_2}\right), \quad (9)$$

$$\omega_e\chi_e = \frac{Be}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right], \quad (10)$$

$$\begin{aligned} & b_1 = \frac{R_ef_3}{3f_2}, \quad b_2 = \frac{R_eb_1f_4}{4f_3}, \\ & b_3 = \frac{R_eb_2f_5}{5f_4}, \quad b_4 = \frac{R_eb_3f_6}{6f_5}, \end{aligned} \quad (11)$$

$$\beta_e = -\frac{12B_e^4}{\omega_e^3}\left(\frac{19}{2} + 9b_1 + \frac{9b_1^2}{2} - 4b_2\right), \quad (12)$$

$$\begin{aligned} \omega_ey_e = & \frac{B_e^2}{2\omega_e}\left(10b_4 - 35b_1b_3 - \frac{17b_2^2}{2}\right. \\ & \left. + \frac{225b_1^2b_2}{4} - \frac{705b_1^4}{32}\right), \end{aligned} \quad (13)$$

$$\begin{aligned} \gamma_e = & \frac{6B_e{}^3}{\omega_e^2}\left(5 + 10b_1 - 3b_2 + 5b_3 - 13b_1b_2\right. \\ & \left. + \frac{15(b_1^2 + b_1^3)}{2}\right), \end{aligned} \quad (14)$$

where B_e is the equilibrium rotational constant, α_e is the vibration–rotation coupling constant, ω_e is the harmonic frequency, $\omega_e\chi_e$ and ω_ey_e are the first-anharmonicity constant and second-anharmonicity constant, β_e is the first centrifugal distortion constant and γ_e is the second rotational constant. The f_2, f_3, f_4, f_5, f_6 are the quadratic, cubic, quartic, quintic and sextic force constants respectively. They can be easily obtained from the APEFs. Then the spectroscopic parameters are determined by the equations.

5. Results and discussion

5.1. The PECs of rare gas complexes

The PECs of the six rare gas complexes are plotted in Fig. 1. All of them have wells although the

one of He_2 is very shallow. This tendency is in good agreement with the previous work of Tang *et al.*[50] The well depth becomes deeper and deeper from He_2 to Ar_2 as the atomic number increases, and Ar_2 has the deepest well among them. The equilibrium distances and dissociation energies of the rare gas complexes are collected in Table 1. From Table 1, we can find that our results improve the agreement with the experimental data in comparison with most other theoretical work in the literatures. Compared with the results of aug-cc-pVQZ of Cybulski *et al.*,[23] we find that using the larger d-aug-cc-pVQZ basis sets increases the dissociation energies although the equilibrium distances are nearly not changed. We also compare the present results with those employing aug-cc-pV5Z which is a basis set adding a polarization function based on aug-cc-pVQZ. The present results are better than those of aug-cc-pV5Z in comparison with the experimental values. Therefore, the diffuse function is more effective on describing the dissociation energy than the polarization function. In addition, our results are better than the ones of Fernández *et al.*,[20] who calculated the Ar_2 complex employing the same basis sets d-aug-cc-pVQZ basis sets but smaller bond functions (3s3p2d1f1g). It means that the larger set of 3s3p2d2f1g bond functions is better than 3s3p2d1f1g for the complexes of rare gases.

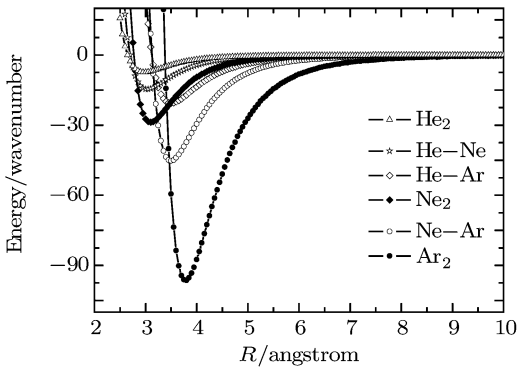


Fig. 1. The PECs of rare gas complexes. Distance in Å (1 Å=0.1 nm), and energy in cm^{-1}. In all computations we adopt the 3s3p2d2f1g bond functions and employ the counterpoise scheme to correct the interaction energy data for BSSE.

Table 1. The equilibrium distances and dissociation energies for the rare gas complexes. BS1 represents d-aug-cc-pVQZ, BS2 represents aug-cc-pVQZ, and BS3 represents aug-cc-pV5Z basis sets. All the three kinds of computations include bond functions of 3s3p2d2f1g.

		He_2	Ne_2	Ar_2	He–Ne	He–Ar	Ne–Ar
R_e/Å	present (BS1)	2.977	3.099	3.782	3.030	3.496	3.495
	CT (BS2)[23]	2.978	3.100	3.783	3.030	3.496	3.496
	CT (BS3)[23]	2.976	3.100	3.779	3.028	3.493	3.493
	others	2.965[52]	3.091[27]	3.783[20]	3.029[18]	3.494[18]	3.489[54]
		2.969[53]	3.091[53]	3.756[53]	3.031[54]	3.480[54]	
	Expt.	2.978[56]	3.094[15]	3.761[13]	3.031[14]	3.480[14]	3.464[16]
			3.1[56]	3.757[55]	3.21[56]	3.51[56]	3.43[56]
			3.758[56]				
D_e/cm^{-1}	present (BS1)	7.397	28.800	97.086	14.646	20.648	45.382
	CT(BS2)[23]	7.377	28.641	96.490	14.578	20.571	45.063
	CT (BS3)[23]	7.390	28.604	96.986	14.610	20.664	45.183
	others	7.660[52]	29.366[27]	96.79[20]	14.595[18]	20.653[18]	46.780[54]
		7.259[53]	29.04[53]	99.21[53]	14.518[54]	20.164[54]	
	Expt.		29.40[15]	99.2[13]	14.655[14]	20.551[14]	45.787[16]
				99.554[55]			

5.2. The APEFs

Using the calculated PECs, we determine the parameters in MS, TT and HUX functions by nonlinear least square fitting. The fitted parameters are listed in Tables 2, 3, and 4, respectively. Comparing the present fitted parameters of TT with the ones of Cybulski *et al.*,[23] we can find that there is a little difference between them. Although we first choose their parameters b, C_6, C_8 and C_{10} fixed as the original fitting ones, all of the ten parameters take part in the process of fitting including b, C_6, C_8 and C_{10} in the end. So our fitting parameters of TT will be more appropriate to the PECs than theirs.

Table 2. The present fitted parameters of TT potential energy function for the rare gas complexes.

TT	He_2	Ne_2	Ar_2	He–Ne	He–Ar	Ne–Ar
A/cm^{-1}	6.6744	83.3446	91.1425	25.6260	22.1715	74.4804
α/a_0^{-1}	1.8869	2.1761	1.4868	2.0602	1.5859	1.7413
β/a_0^{-2}	–0.0638	–0.0285	–0.0338	–0.0331	–0.0463	–0.0379
b/a_0^{-1}	1.8636	1.8587	1.6802	2.9406	2.4536	1.6355
$C_6/E_\mathrm{h}a_0^6$	1.4604	6.1096	64.8044	3.0409	9.8890	18.43386
$C_8/E_\mathrm{h}a_0^8$	14.0200	106.7057	1.532×10^3	35.4988	147.7835	497.4372
$C_{10}/E_\mathrm{h}a_0^{10}$	183.9732	1.747×10^3	4.748×10^4	421.4117	2.225×10^3	1.092×10^4
$C_{12}/E_\mathrm{h}a_0^{12}$	3.393×10^3	2.758×10^4	1.983×10^6	5.230×10^3	3.472×10^4	2.007×10^5
$C_{14}/E_\mathrm{h}a_0^{14}$	8.571×10^4	4.092×10^5	1.088×10^8	6.616×10^4	5.470×10^5	3.009×10^6
$C_{16}/E_\mathrm{h}a_0^{16}$	2.888×10^6	5.554×10^6	7.640×10^9	8.304×10^5	8.473×10^6	3.582×10^7

Table 3. The present fitted parameters of MS potential energy function for the rare gas complexes.

MS	He_2	Ne_2	Ar_2	He–Ne	He–Ar	Ne–Ar
$a_1/\mathrm{Å}^{-1}$	1.8133	2.0265	1.7598	2.0393	1.5985	1.6436
$a_2/\mathrm{Å}^{-2}$	–2.6848	–2.1907	–1.2948	–2.1691	–1.9993	–2.0036
$a_3/\mathrm{Å}^{-3}$	2.7652	2.1882	0.9367	2.1215	1.7700	1.7740
$a_4/\mathrm{Å}^{-4}$	–1.8043	–1.3344	–0.3296	–1.2016	–0.9996	–1.0164
$a_5/\mathrm{Å}^{-5}$	0.8487	0.6637	0.0916	0.4945	0.4169	0.4417
$a_6/\mathrm{Å}^{-6}$	–0.2672	-0.2350	–0.0176	-0.1124	–0.1185	–0.1314
$a_7/\mathrm{Å}^{-7}$	0.0527	0.0558	0.0034	0.0105	0.0214	0.0245
$a_8/\mathrm{Å}^{-8}$	–0.0057	–0.0077	–0.0005	0.0005	–0.0022	–0.0025
$a_9/\mathrm{Å}^{-9}$	0.0003	0.0005	0.0001	–0.0005	0.00009	0.00011

Table 4. The present fitted parameters of HUX potential energy function for the rare gas complexes.

HUX	He_2	Ne_2	Ar_2	He–Ne	He–Ar	Ne–Ar
A/cm^{-1}	1.744×10^3	1.407×10^3	7.184×10^7	0.443	994.818	21.240
$a_1/\mathrm{Å}^{-1}$	–91.369	–275.909	1.389	82.208	–261.474	–140.474
$a_2/\mathrm{Å}^{-2}$	25.467	25.063	–0.661	–33.512	30.459	108.431
$a_3/\mathrm{Å}^{-3}$	–3.980	3.437	0.068	–0.025	–36.100	–3.140
$a_4/\mathrm{Å}^{-4}$	3.295	3.174	2.974	1.161	3.195	1.813
R_m/a_0	2.962	2.997	3.783	3.035	3.493	3.495
$C_6/E_\mathrm{h}a_0^6$	5.733×10^3	1.244×10^4	2.636×10^5	-1.600×10^4	3.396×10^4	3.161×10^4
$C_8/E_\mathrm{h}a_0^8$	1.112×10^5	1.059×10^6	5.950×10^6	7.970×10^5	1.265×10^6	6.160×10^6
$C_{10}/E_\mathrm{h}a_0^{10}$	-1.86×10^6	-1.218×10^7	-5.095×10^7	-4.971×10^6	-2.303×10^7	5.926×10^7

As can be seen in Table 5, all the RMSs are very small, and the RMSs using MS function are smaller than those using TT or HUX function in some cases. It implies that the fitting process is of high accuracy and all the three expressions can well reproduce the PECs of the rare gas complexes. Although the MS function has no explicit representation of long range potential which is different from that using TT and HUX functions, it also can provide good description for the PECs of the rare gas complexes.

Table 5. The RMSs of the MS, TT and HUX functions. The unit is in cm^{-1}.

	He_2	Ne_2	Ar_2	He–Ne	He–Ar	Ne–Ar
TT	4.295×10^{-4}	1.616×10^{-3}	4.884×10^{-3}	8.705×10^{-4}	1.263×10^{-3}	1.314×10^{-3}
MS	1.797×10^{-4}	1.197×10^{-3}	7.430×10^{-3}	6.926×10^{-4}	2.776×10^{-3}	4.348×10^{-3}
HUX	1.355×10^{-4}	1.466×10^{-3}	4.763×10^{-3}	7.807×10^{-4}	6.347×10^{-4}	1.376×10^{-3}

5.3. The spectroscopic parameters

Employing the equations for the relationship between the force constants and spectroscopic parameters, we calculated the force constants using the fitted APEFs and then obtained the spectroscopic parameters B_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, γ_e and β_e. The results are collected in Table 6. Our results are close to several spectroscopic parameters reported by Herman *et al.*[13] and Olgivie *et al.*[53,54] The more spectroscopic parameters determined by the present work can serve as a guide for further studies on this system. We also compare the spectroscopic parameters which are calculated from the three different fitted APEFs and they are in agreement with each other. It confirms again that all the three expressions can describe the van der Waals interactions between rare gas atoms.

Table 6. The spectroscopic parameters of the rare gas complexes. All the parameters are in cm^{-1}.

	method	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	β_e
He_2	MS	33.640	41.234	3.928	1.320	0.974	0.630	0.012
	TT	33.276	40.083	3.536	1.322	0.975	0.611	0.012
	HUX	33.517	40.887	4.059	1.323	0.979	0.623	0.012
		33.20[53]						
		35.02[57]						
Ne_2	MS	28.597	8.069	0.206	0.178	0.037	5.567×10^{-3}	2.231×10^{-5}
	TT	28.529	8.070	0.201	0.178	0.038	5.746×10^{-3}	2.246×10^{-5}
	HUX	28.686	8.135	0.197	0.178	0.037	5.613×10^{-3}	2.252×10^{-5}
	Ref.	28.52[53]						
		32.80[57]						
Ar_2	MS	30.456	2.648	0.005	0.059	0.004	2.035×10^{-4}	2.372×10^{-7}
	TT	30.304	2.612	0.008	0.059	0.004	1.926×10^{-4}	2.336×10^{-7}
	HUX	30.438	2.640	0.007	0.059	0.004	1.993×10^{-4}	2.359×10^{-7}
	Ref.	30.69[13]	2.425[13]	0.062[13]	0.060[13]	0.004[13]	3.23×10^{-4}[13]	
		30.95[53]	2.561[58]		0.060[27]	0.004[27]	3.13×10^{-4}[27]	
		30.68[58]						
		20.44[57]						
He–Ne	MS	35.682	24.366	1.406	0.614	0.296	0.107	1.094×10^{-3}
	TT	35.446	24.039	1.180	0.614	0.296	0.106	1.089×10^{-3}
	HUX	35.469	24.087	1.419	0.615	0.297	0.103	1.080×10^{-4}
	Ref.	34.96[54]						
		53.31[57]						
He–Ar	MS	35.471	17.074	0.566	0.401	0.141	3.728×10^{-2}	2.563×10^{-4}
	TT	35.436	16.918	0.556	0.401	0.141	3.643×10^{-3}	2.528×10^{-4}
	HUX	35.487	17.139	0.578	0.401	0.142	3.752×10^{-3}	2.577×10^{-4}
	Ref.	34.82[54]						
		39.49[57]						
Ne–Ar	MS	27.681	4.749	0.058	0.104	0.013	1.268×10^{-3}	3.007×10^{-6}
	TT	27.643	4.719	0.049	0.104	0.013	1.271×10^{-3}	2.989×10^{-6}
	HUX	27.643	4.727	0.065	0.104	0.013	1.229×10^{-3}	2.984×10^{-6}
	Ref.	26.16[54]						

6. Conclusion

In this article, the PECs of six rare gas complexes are calculated by using the CCSD(T) method and d-aug-cc-pVQZ basis set with the bond functions of 3s3p2d2f1g. Compared with the experimental values, we find that diffuse functions can improve the calculation of dissociation energies. It also finds that the diffuse function is more effective than polarization function on describing the weak interactions for the complexes of rare gases. The larger bond functions of 3s3p2d1f1g also affect improving the PECs.

The MS, TT and HUX expressions of APEF are found to reproduce the PECs well. In particular, MS function can represent the weak interactions although it has not explicit terms of long range interaction. The determined spectroscopic parameters based on the present APEFs are consistent with the reported values

available in the literatures, which confirm the high quality of the APEF. Therefore the APEFs can be used for more investigations to understand the interactions between rare gas atoms.

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