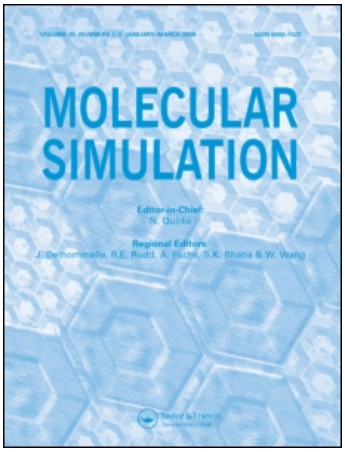

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Accurate *ab initio* calculation of the Ar-CF_4 intermolecular potential energy surface

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Accurate *ab initio* calculation of the Ar—CF_4 intermolecular potential energy surface

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Ar—CF_4 intermolecular interaction potential is studied by *ab initio* calculations at the MP2 and CCSD(T) levels of theory containing the so-called bond functions ({3s3p2d1f} basis set was chosen) both with and without a correction for the basis-set superposition error. The calculations were performed with Dunning's correlation consistent basis sets (aug-cc-pVXZ, X = D, T, Q, 5) to extrapolate the Ar—CF_4 potential energy minimum and intermolecular distance to their complete basis set (CBS) limits. It is shown that the addition of bond functions results in a dramatic improvement in the convergence of the calculated interaction energies at the MP2/aug-cc-pVTZ level. The MP2/{3s3p2d1f}-aug-cc-pVTZ potential energy surface even approaches the CCSD(T)/aug-cc-pVQZ potential energy surface. The potential energy minima and the intermolecular distances are both significantly closer to the CBS limit when using the bond functions, and it implies that adding bond functions in the calculation has a great effect on the interaction energies. We also find that with bond functions included in the CCSD(T)/aug-cc-pVDZ model chemistry, the potential energy minima are extremely close to the CBS limit and are better than the CCSD(T)/aug-cc-pVQZ values. Several levels of theory described in the text were used to determine pairwise analytic potential energy surfaces for Ar + CF_4. The analytic potential energy surfaces are in very good agreement with the *ab initio* values.

Keywords: bond functions; dispersion interaction; complete basis set; focal-point method; CCSD(T) and MP2 theories

1. Introduction

Fluorine-containing molecules are of high importance in numerous fields of chemistry. For example, perfluoroalkanes are used as solvents in organic synthesis and oxygen-carrying blood substitutes [1,2]; the energy-transfer dynamics associated with rare gas atom collisions with fluorocarbon self-assembled monolayer (SAM) surfaces are studied in chemical dynamic simulations [3–5]. The liquid and thermodynamic properties of these fluorine-containing molecules are dominated by their intermolecular interactions. Therefore, detailed studies on the van der Waals non-bonding interactions of rare gas atoms and fluorocarbon are indispensable. To understand the efficiency of collisional energy transfer of rare gases from organic surfaces is important for the categories of interfacial chemistry at the atomic level [4,6–8]. Many experiments (e.g. molecular beam scattering) have studied the dynamics of collisions of rare gases with both alkanethiol H-SAM and F-SAM absorbed on a gold surface [3,9–15]. For collisions of the impinging rare gas atoms, a fluorinated terminated SAM absorbs less amount of energy than a hydrogenated SAM. This indicates that the characteristic of a F-SAM surface is more rigid than that of a H-SAM surface. Generally, multiparametric analytic functions used in chemical dynamics simulations for potential energy surfaces are fitted to their intermolecular interaction values from *ab initio* calculations [16,17]. There exist various experimental methods to measure the intermolecular interactions of fluorine-containing molecules, but it is still difficult to accurately evaluate the magnitude and orientation dependence of this interaction solely from experiments.

Along with the progress of the computational facilities, *ab initio* molecular orbital calculation is becoming an effective tool to study intermolecular interactions [18,19]. *Ab initio* calculations could provide accurate estimates of the intermolecular interaction energy with high level of theories for correcting electron correlation effect and considerable basis functions in the basis sets used [20–22]. However, it requires plenty of computational resources and a huge amount of CPU time. Furthermore, the extremely accurate interaction energies, especially for the minimum region of the potential energy surface, sometimes are not sufficient compared to their complete basis-set (CBS) limit values. Hence, we make use of the bond functions method proposed by Tao et al. [23–33] to improve the results. The bond functions have been used to calculate the van der Waals interaction potentials of symmetric and asymmetric pairs of rare gas dimers (e.g. Ar_2 [30] and He—Ar [28]), rare gas–molecule complexes

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(e.g. He—H_2O [25] and Ar—NH_3 [31]) and molecule–molecule complexes (e.g. HCl dimer [32] and NH_3 dimer [33]). Now, we carry out the study of the intermolecular interaction potential of Ar—CF_4 rare gas–molecule complexes using bond functions. To the best of our knowledge, no such case has been reported, as yet. One purpose of this study is to determine the level of theories, the size of basis sets and with or without bond functions that are required to calculate accurate Ar—CF_4 intermolecular potentials. An additional goal of this paper is using the *ab initio* data to derive the Ar—CF_4 pairwise analytic potential energy surfaces that might be applied to chemical dynamics simulations of collisions of rare gases with fluorocarbon surfaces [17,34–36].

2. Theoretical calculations

Interaction energies were performed using second-order Møller–Plesset perturbation theory (MP2) as well as coupled-cluster singles and doubles method incorporating a perturbative correction for triples (CCSD(T)). The geometry of the CF_4 monomer was optimised at the MP2/6-31G* level; in this work, for the Ar—CF_4 intermolecular potential calculations, the CF_4 molecule has been held fixed in its equilibrium geometry (r(C–F) = 1.33058 Å). Dunning's correlation consistent basis sets (aug-cc-pVXZ, X = D, T, Q, 5) were used [37]. Electron correlation that excluded the core electrons was treated by the MP2 and CCSD(T) levels of theory. The basis-set superposition error (BSSE) was corrected for in all calculations using the standard counterpoise method [38]. The exponents of the {3s3p2d1f} bond functions are 0.9, 0.3 and 0.1 for 3s and 3p; 0.6 and 0.2 for 2d; and 0.3 for 1f. The {3s3p2d1f} bond functions are denoted as 'bf' hereafter.

The Ar—CF_4 intermolecular potential energy surfaces and their minima were calculated by scanning the coordinate of Ar—C atoms; the separation between the points is 0.1 Å, except that at the potential well-depth region, it is 0.05 Å. Two orientations of Ar—CF_4 were investigated for the intermolecular potential energy curves: both orientations are C_{3v} symmetric with the Ar atom collinear with a C—F bond. For one curve, identified as face Ar + F_3C—F, Ar approaches a CF_3 face of CF_4 tetrahedra; for the other curve, referred to as vertex Ar + F—CF_3, Ar is along an F atom of the tetrahedra. The potential energy minima are denoted by ε, and the Ar—C separations at the potential energy minima (ε) are denoted by R_0. The MP2/aug-cc-pVXZ (where X = D, T, Q, 5) and CCSD(T)/aug-cc-pVXZ (where X = D, T, Q) levels of theory were used to determine the R_0 and ε values for the two Ar—CF_4 curves. The {3s3p2d1f} bond functions were placed at the midpoint between the Ar and C atoms for Ar + F_3C—F, and between the Ar and F atoms for Ar + F—CF_3. The GAUSSIAN 03 [39] program was used for all *ab initio* molecular orbital calculations both with and without a correction for the BSSE and bond functions.

Both the MP2 and CCSD(T) total energies were extrapolated to the CBS limit. Two extrapolation methods were widely applied. One of the formulae used is that proposed by Halkier et al. [40] and is denoted as CBS(T,Q) or CBS(Q,5):

$$E_{XY}^{\infty} = \frac{X^3 E_X^{\text{corr}} - Y^3 E_Y^{\text{corr}}}{X^3 - Y^3}, \tag{1}$$

assuming that we have carried out two calculations with cardinal numbers X and Y and obtained the energies E_X^{corr} and E_Y^{corr}, respectively, where X represents the aug-cc-pVXZ basis set ($X = 2, 3, 4, 5$), and the relationship between the two cardinal numbers X and Y is $X = Y + 1$.

The other method is developed from Peterson et al. [41] in the form of a mixed exponential/Gaussian function: $E(n) = E_{\text{CBS}} + A\exp[-(n-1)]B\exp[-(n-1)^2]$, where n represents the aug-cc-pVnZ basis set ($n = 2, 3, 4, 5$). From our calculations, the CBS limits estimated by the two extrapolation methods are nearly equal; with BSSE correction, the CBS limits derived from the former method have smaller potential energy minimum and intermolecular distance than those from the latter method. For our calculations in this article, Equation (1) was chosen as the CBS limit extrapolation function.

3. Results

3.1 Comparison of MP2 and CCSD(T) interaction energies

Table 1 lists the intermolecular interaction energies calculated by the MP2 and CCSD(T) methods with the same aug-cc-pVTZ basis set (CCSD(T)-bf with the aug-cc-pVDZ basis set) for the face Ar + F_3C—F configuration. Our calculations are not in complete agreement with those of Vayner [35], probably due to the small difference in the CF_4 geometry. Nevertheless, the MP2 results are in good agreement with the CCSD(T) results for each Ar—C distance on the Ar + F_3C—F potential energy surface, and the average relative error with and without BSSE correction between the MP2 and CCSD(T) values are merely about 1.6 and 1.5%, respectively. The intermolecular interaction energies for the vertex Ar + F—CF_3 configuration were also calculated at the MP2 and CCSD(T) levels with the aug-cc-pVTZ basis set (CCSD(T)-bf with the aug-cc-pVDZ basis set); the results are listed in Table 2. Similar results were obtained for the vertex Ar + F—CF_3 configuration intermolecular interaction energies. The MP2/aug-cc-pVTZ and CCSD(T)/ aug-cc-pVTZ potential energy curves with BSSE correction for the two Ar + CF_4 configurations are

Table 1. MP2 and CCSD(T) theories for the face Ar + F_3C—F potential energy surface with and without BSSE correction, and with and without bond functions[a].

	MP2		CCSD(T)		MP2-bf[b]	CCSD(T)-bf[b,c]	MP2-CBS(T,Q)[d]
Ar—C	No corr.	With corr.	No corr.	With corr.	With corr.	With corr.	With corr.
2.00	145.577	148.645	147.492	150.689	147.021	154.271	142.860
2.30	54.069	56.072	54.819	56.910	55.125	58.122	53.264
2.60	17.663	18.945	17.914	19.247	18.420	19.544	17.652
2.90	4.630	5.425	4.688	5.511	5.128	5.470	4.815
3.10	1.347	1.925	1.355	1.953	1.715	1.833	1.540
3.30	−0.064	0.368	−0.076	0.370	0.215	0.230	0.115
3.50	−0.585	−0.252	−0.602	−0.259	−0.365	−0.390	−0.424
3.60	−0.676	−0.381	−0.692	−0.390	−0.479	−0.511	−0.524
3.65	−0.696	−0.419	−0.712	−0.427	−0.509	−0.542	−0.548
3.70	−0.703	−0.443	−0.719	−0.452	−0.527	−0.560	−0.561
3.75	−0.701	−0.457	−0.716	−0.465	−0.534	−0.567	−0.564
3.80	−0.691	−0.462	−0.706	−0.470	−0.533	−0.565	−0.559
3.85	−0.676	−0.460	−0.689	−0.468	−0.526	−0.556	−0.549
3.90	−0.656	−0.454	−0.669	−0.461	−0.514	−0.543	−0.534
4.00	−0.609	−0.431	−0.620	−0.436	−0.482	−0.505	−0.491
4.20	−0.504	−0.364	−0.512	−0.368	−0.400	−0.415	−0.407
4.40	−0.406	−0.295	−0.410	−0.297	−0.319	−0.327	−0.322
4.60	−0.322	−0.234	−0.325	−0.235	−0.250	−0.253	−0.251
4.80	−0.255	−0.184	−0.256	−0.184	−0.195	−0.195	−0.195
5.00	−0.202	−0.144	−0.202	−0.144	−0.152	−0.150	−0.151

[a] The aug-cc-pVTZ basis set was used for all the calculations except those with the CCSD(T)-bf method. Energies are in kcal/mol, and Ar—C distances are in Å. [b] With {3s3p2d1f} bond functions at the midpoint between Ar and C atoms. [c] The aug-cc-pVDZ basis set was used. [d] CBS is the complete basis-set limit.

Table 2. MP2 and CCSD(T) theories for the vertex Ar + F—CF_3 potential energy surface with and without BSSE correction, and with and without bond functions[a].

	MP2		CCSD(T)		MP2-bf[b]	CCSD(T)-bf[b,c]	MP2-CBS(T,Q)[d]
Ar—C	No corr.	With corr.	No corr.	With corr.	With corr.	With corr.	With corr.
3.00	126.520	128.662	128.138	130.368	127.567	132.421	124.583
3.30	39.770	40.980	40.355	41.610	40.286	41.927	39.176
3.60	11.134	11.868	11.312	12.074	11.488	12.004	11.081
3.90	2.449	2.911	2.485	2.963	2.719	2.844	2.574
4.10	0.557	0.898	0.561	0.912	0.775	0.801	0.705
4.30	−0.159	0.095	−0.166	0.094	0.015	0.001	−0.018
4.50	−0.375	−0.184	−0.385	−0.190	−0.238	−0.263	−0.253
4.55	−0.392	−0.214	−0.402	−0.219	−0.262	−0.288	−0.274
4.60	−0.400	−0.233	−0.409	−0.238	−0.277	−0.303	−0.287
4.65	−0.401	−0.244	−0.410	−0.250	−0.285	−0.310	−0.292
4.70	−0.396	−0.250	−0.406	−0.255	−0.286	−0.311	−0.293
4.75	−0.388	−0.250	−0.397	−0.256	−0.284	−0.308	−0.289
4.80	−0.378	−0.248	−0.386	−0.253	−0.278	−0.302	−0.283
4.90	−0.351	−0.235	−0.359	−0.240	−0.261	−0.282	−0.264
5.00	−0.322	−0.218	−0.329	−0.221	−0.239	−0.258	−0.241
5.20	−0.264	−0.178	−0.269	−0.180	−0.193	−0.207	−0.194
5.40	−0.214	−0.141	−0.218	−0.143	−0.152	−0.160	−0.152
5.60	−0.173	−0.111	−0.176	−0.112	−0.118	−0.123	−0.118
5.80	−0.139	−0.087	−0.142	−0.088	−0.092	−0.094	−0.092
6.00	−0.112	−0.069	−0.114	−0.069	−0.072	−0.073	−0.072

[a] The aug-cc-pVTZ basis set was used for all the calculations except those with the CCSD(T)-bf method. Energies are in kcal/mol, and Ar—C distances are in Å. [b] With {3s3p2d1f} bond functions at the midpoint between the Ar and F atoms, collinear with Ar—C. [c] The aug-cc-pVDZ basis set was used. [d] CBS is the complete basis-set limit.

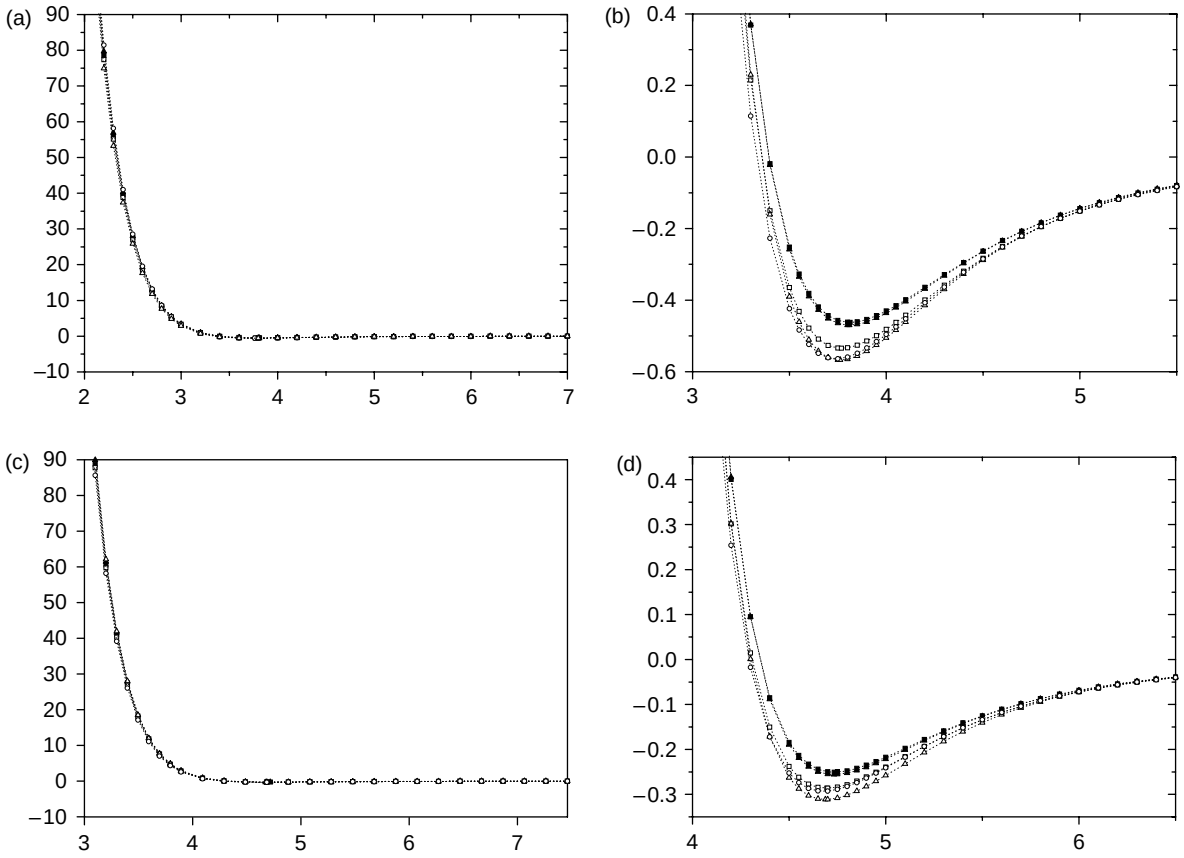

Figure 1. (a) Face Ar + F_3C—F potential energy curves for a full energy range. (b) Face Ar + F_3C—F potential energy curves for the well region. (c) Vertex Ar + F—CF_3 potential energy curves for a full energy range. (d) Vertex Ar + F—CF_3 potential energy curves for the well region. Calculated intermolecular potential energy (in kcal/mol) as a function of the Ar—C distance (in Å). All calculations include BSSE correction. Filled squares, MP2/aug-cc-pVTZ potentials; filled triangles, CCSD(T)/aug-cc-pVTZ potentials; open squares, MP2/bf-aug-cc-pVTZ potentials; open triangles, CCSD(T)/bf-aug-cc-pVDZ potentials; open circles, MP2/CBS potentials.

shown in Figure 1. As shown in the figure, the MP2 potential energy curves nearly coincide with the CCSD(T) curves, and the latter have smaller energies in the minimum region. The MP2/aug-cc-pVTZ potential energy minima ε and R_0 values with and without BSSE correction are very close to the CCSD(T)/aug-cc-pVTZ values for both configurations. The MP2 potential energy minima ε values are at most 0.016 kcal/mol higher and the R_0 values are within 0.003 Å larger than the corresponding CCSD(T) values. Thus, calculations with MP2 theory not only afford accurate intermolecular potentials for the two Ar + CF_4 configurations but also require considerably less computational resources than the CCSD(T) theory [42].

Tables 1 and 2 also list the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ potential energies with BSSE correction and bond functions for the Ar + F_3C—F and Ar + F—CF_3 configurations, respectively; both potential energy curves are also shown in Figure 1. As shown in Figure 1(b) and (d), the potential energy curves in the minima region with the bond functions are appreciably deeper than those without the bond functions, that is to say, the interaction energies in the minima region with BSSE correction calculated at the MP2/bf-aug-cc-pVTZ level are lower than those calculated without bond functions added to the MP2 and CCSD(T) theories with the same basis set. The MP2/bf-aug-cc-pVTZ potential energy minima for the face and vertex orientations are improved by 15.6 and 13.9%, respectively, compared to the MP2/aug-cc-pVTZ values calculated without bond functions. The lowest interaction energies were obtained at the CCSD(T)/bf-aug-cc-pVDZ level; the potential energy minima of the two orientations were enhanced by about 70% over those at the CCSD(T)/aug-cc-pVDZ level and by 20% over those at the CCSD(T)/aug-cc-pVTZ level without bond functions added. Such considerable differences would indeed influence the derived Ar + CF_4 potential functions applied to simulate collisions of the Ar atom with the CF_4 molecule. The applicability of adding the bond function basis set to the MP2 and CCSD(T) theories in the systems is discussed later.

3.2 Ar + F_3C—F and Ar + F—CF_3 potential energy minima

Accurate energy and geometry of MP2 and CCSD(T) van der Waals minima with and without BSSE correction, and with and without bond functions for the two Ar + CF_4 configurations are listed in Table 3. The values listed in the table were calculated at each R_0 value determined from the potential energy curve for each individual model chemistry; MP2 theory up to aug-cc-pV5Z and CCSD(T) theory up to aug-cc-pVQZ. Calculations with BSSE correction lead to larger ε and R_0 values than those without BSSE correction. Energies of aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z were fitted with Equation (1) to estimate the CBS limits – CBS(T,Q) and CBS(Q,5) – for the Ar + F_3C—F and Ar + F—CF_3 potential energy minima, respectively. The CBS limits for the potential energy minima at the MP2 and CCSD(T) levels of theory are all very close both with and without BSSE corrections and with and without bond functions. Therefore, the calculations performed with bond functions and the extrapolation to the CBS limit are reliable. As expected, the potential energy minima approach the CBS values as the number of basis functions increases. With BSSE correction at the MP2 theory, the potential energy minima differences compared to the CBS(T,Q) limit of CCSD(T) theory with BSSE correction and without bond functions (hereafter denoted as CC-CBS) for the basis sets aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z are 42.0, 20.8, 11.0 and 7.5%, respectively, for face Ar + F_3-C—F; 37.7, 16.9, 9.3 and 5.3%, respectively, for vertex Ar + F—CF_3. The trend for the corresponding calculations at the CCSD(T) theory is similar to the MP2 method, and the potential energy minima differences compared to CC-CBS for the basis sets aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ are 43.2, 19.4 and 8.2%, respectively, for face Ar + F_3C—F; 38.4, 15.2 and 6.3%, respectively, for vertex Ar + F—CF_3. With bond functions included in the MP2 calculations, the potential energy minima for the basis sets aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z would approach 89.5, 91.6, 93.7 and 95.0%, respectively, of the CC-CBS value for face Ar + F_3C—F; 94.4, 94.7, 96.4 and 97.4%, respectively, for vertex Ar + F—CF_3. Calculations with bond functions at the CCSD(T) theory have achieved excellent performance in the potential energy minima values, and for the basis sets aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ are 97.3, 96.6 and 97.3%, respectively, of the CC-CBS value for face Ar + F_3C—F; 103.0, 100.0 and 100.3%, respectively, for vertex Ar + F—CF_3.

Table 3. Energy and geometry of MP2 and CCSD(T) van der Waals minima with and without BSSE correction, and with and without bond functions[a].

Theory	BSSE		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	CBS(T,Q)	CBS(Q,5)
Ar + F_3C—F potential curve								
MP2	No corr.	R_0	3.700	3.712	3.720	3.727	3.726	3.734
		ε	−0.716	−0.703	−0.644	−0.619	−0.601	−0.592
	Corr.	R_0	3.949	3.813	3.771	3.757	3.740	3.742
		ε	−0.338	−0.462	−0.519	−0.539	−0.561	−0.560
CCSD(T)	No corr.	R_0	3.689	3.709	3.717		3.723	
		ε	−0.761	−0.719	−0.650		−0.599	
	Corr.	R_0	3.959	3.810	3.762		3.727	
		ε	−0.331	−0.470	−0.535		−0.583	
MP2-bf	Corr.	R_0	3.781	3.769	3.755	3.748	3.745	3.741
		ε	−0.522	−0.534	−0.546	−0.554	−0.554	−0.562
CCSD(T)-bf	Corr.	R_0	3.762	3.757	3.746		3.738	
		ε	−0.567	−0.563	−0.567		−0.571	
Ar + F—CF_3 potential curve								
MP2	No corr.	R_0	4.687	4.632	4.652	4.657	4.667	4.662
		ε	−0.423	−0.401	−0.354	−0.335	−0.320	−0.316
	Corr.	R_0	4.848	4.734	4.703	4.687	4.680	4.670
		ε	−0.188	−0.251	−0.274	−0.286	−0.292	−0.298
CCSD(T)	No corr.	R_0	4.685	4.630	4.651		4.666	
		ε	−0.446	−0.411	−0.355		−0.314	
	Corr.	R_0	4.860	4.732	4.697		4.671	
		ε	−0.186	−0.256	−0.283		−0.302	
MP2-bf	Corr.	R_0	4.705	4.695	4.684	4.678	4.676	4.672
		ε	−0.285	−0.286	−0.291	−0.294	−0.295	−0.297
CCSD(T)-bf	Corr.	R_0	4.688	4.684	4.677		4.672	
		ε	−0.311	−0.302	−0.303		−0.303	

[a] Well depths (ε) are in kcal/mol, and Ar—C distances (R_0) are in Å. The calculations were performed at each R_0 value determined from individual model chemistry potential energy curves. cc-pVXZ (X = D, T, Q, 5) refers to Dunning's aug-cc-pVXZ (X = D, T, Q, 5) basis sets. CBS is the complete basis-set limit.

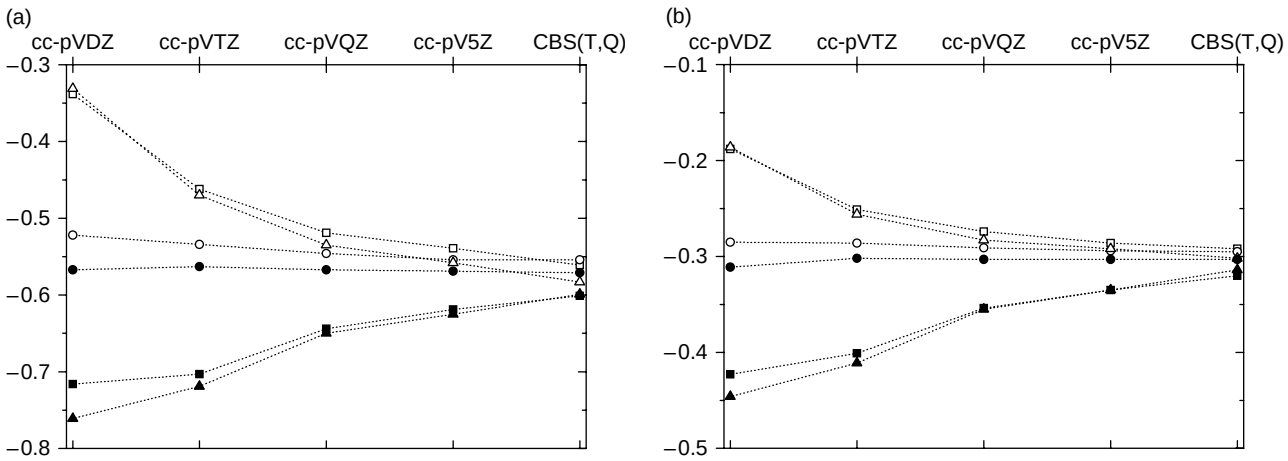

Figure 2. (a) Basis-set dependence of the face Ar + F_3C—F van der Waals minima (ε). (b) Basis-set dependence of the vertex Ar + F—CF_3 van der Waals minima (ε). Energies are in kcal/mol. Filled squares, results of MP2 theory without BSSE correction; open squares, MP2 theory with BSSE correction; filled triangles, CCSD(T) theory without BSSE correction; open triangles, CCSD(T) theory with BSSE correction; open circles, MP2 theory with bond functions and BSSE correction; filled circles, CCSD(T) theory with bond functions and BSSE correction. The CCSD(T)/aug-cc-pV5Z and CCSD(T)/bf-aug-cc-pV5Z values were estimated from Equation (1).

The intermolecular interaction energies calculated by the MP2/CBS(T,Q) [36] method for the two Ar + F_3C—F and Ar + F—CF_3 configurations are listed in Tables 1 and 2, and their potential energy surfaces are shown in Figure 1. The MP2/bf-aug-cc-pVTZ and CCSD(T)/bf-aug-cc-pVDZ potential energy curves are close to the MP2/CBS(T,Q) potential energy curves. It emphasises the importance of the electron correlation treated by the MP2 and CCSD(T) levels of theory and implies that adding bond functions in the calculations could easily approach the CBS limit even with small basis sets, especially for those at the well-depth region that are of high concern. The basis-set dependences of the two Ar + CF_4 potential energy minima are shown in Figure 2. The CCSD(T)/aug-cc-pV5Z values with and without BSSE correction, and with and without bond functions were estimated from Equation (1). The differences in potential energy minima between the CCSD(T) and MP2 levels with BSSE correction increase as the quality of basis sets is enhanced, implying that MP2 results with larger basis sets might not be suitable approximations of CCSD(T) results for intermolecular interaction energies. For the two Ar + CF_4 potential energy curves with BSSE correction, CCSD(T) has lower potential energy minima than MP2 for all basis sets used

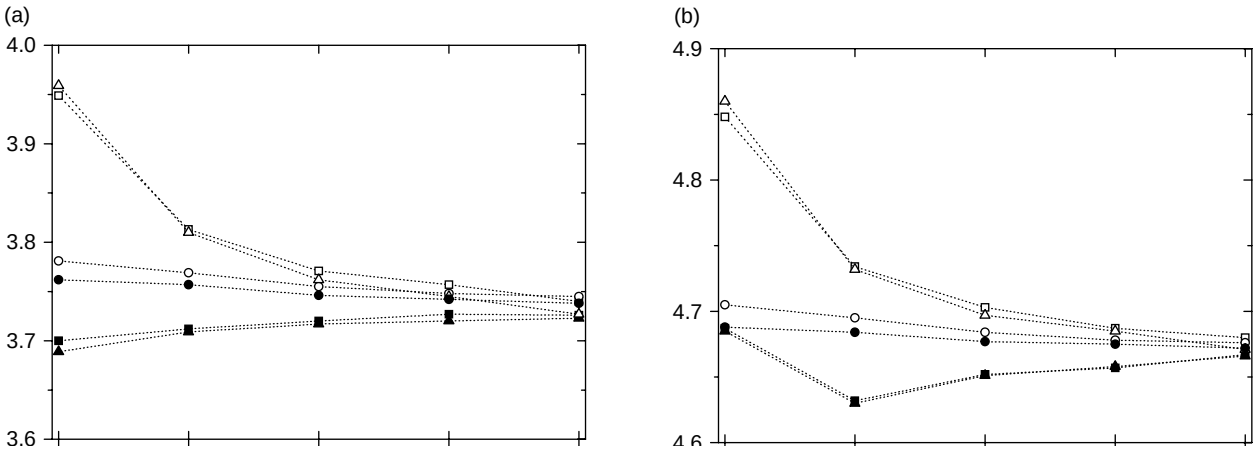

Figure 3. (a) Basis-set dependence of the face Ar + F_3C—F van der Waals minima Ar—C distance (R_0). (b) Basis-set dependence of the vertex Ar + F—CF_3 van der Waals minima Ar—C distance (R_0). Distances are in Å. Filled squares, results of MP2 theory without BSSE correction; open squares, MP2 theory with BSSE correction; filled triangles, CCSD(T) theory without BSSE correction; open triangles, CCSD(T) theory with BSSE correction; open circles, MP2 theory with bond functions and BSSE correction; filled circles, CCSD(T) theory with bond functions and BSSE correction. The CCSD(T)/aug-cc-pV5Z and CCSD(T)/bf-aug-cc-pV5Z values were estimated from Equation (1).

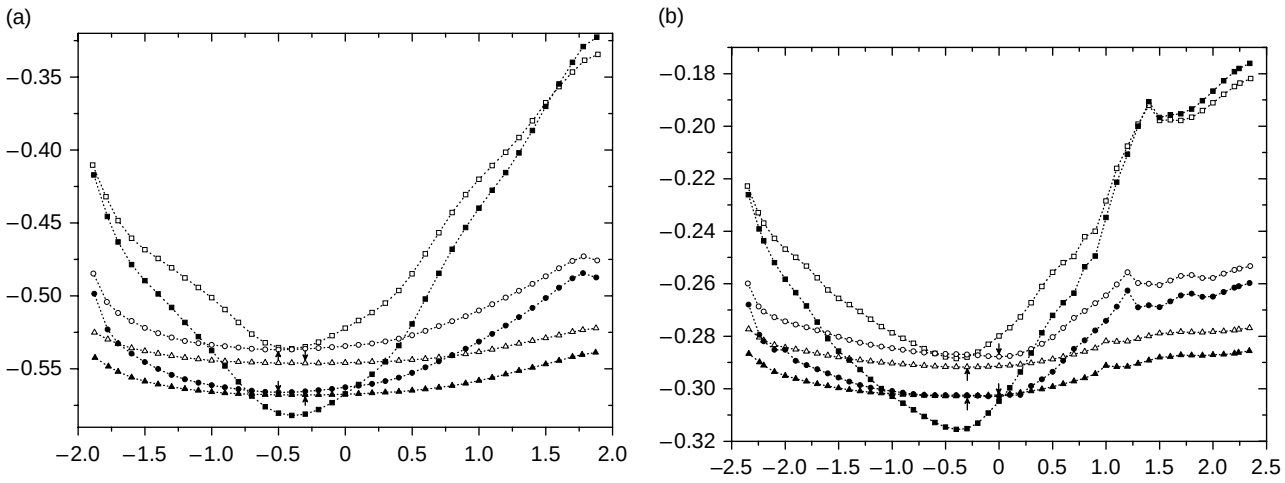

Figure 4. (a) Basis-set dependence of the face Ar + F_3C—F intermolecular potential energy vs. bond functions location. (b) Basis-set dependence of the vertex Ar + F—CF_3 intermolecular potential energy vs. bond function location. Calculated intermolecular potential energy (in kcal/mol) as a function of the distance (in Å) between bond functions and the Ar—C midpoint. All calculations include BSSE correction. Open squares, MP2/bf-aug-cc-pVDZ potentials; open circles, MP2/bf-aug-cc-pVTZ potentials; open triangles, MP2/bf-aug-cc-pVQZ potentials; filled squares, CCSD(T)/bf-aug-cc-pVDZ potentials; filled circles, CCSD(T)/bf-aug-cc-pVTZ potentials; filled triangles, CCSD(T)/bf-aug-cc-pVQZ potentials. The arrows indicate the positions which are the lowest points of individual model chemistry potential energy curves.

except aug-cc-pVDZ. As shown in Figure 2, the potential energy minima slowly converge to their CBS limits for the Ar + F_3C—F and Ar + F—CF_3 configurations with and without BSEE correction. However, it is clear that adding bond functions to the MP2 calculation with BSSE correction causes the potential energy minima to converge dramatically fast to the CBS limit even with the smallest aug-cc-pVDZ basis set; the largest differences from CC-CBS for the Ar + F_3C—F and Ar + F—CF_3 orientations are only 0.061 and 0.017 kcal/mol, respectively. Similar calculations to the CCSD(T) theory show that the largest differences from CC-CBS for the Ar + F_3C—F and Ar + F—CF_3 configurations are merely 0.02 and 0.009 kcal/mol, respectively. Note that the potential energy minima calculated by the CCSD(T)/bf-aug-cc-pVDZ level for the two Ar + CF_4 configurations are slightly too small; probably the number of basis functions of the aug-cc-pVDZ basis set is not adequate for the CCSD(T) calculations with bond functions.

As shown in Table 3, the R_0 values from aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z were also fitted to determine their R_0 CBS limit values; the basis set dependence of the R_0 values for the two configurations are shown in Figure 3. Similarly, R_0 values for CCSD(T)/aug-cc-pV5Z with and without BSSE correction, and with and without bond functions were estimated from Equation (1). As before, all the R_0 CBS limits for both theories are very close to both with and without BSSE corrections and with and without bond functions. As shown in Figure 3, R_0 slowly converges to the CBS limit for both configurations with and without BSEE correction. Again, adding bond functions to the MP2 and CCSD(T) calculations with BSSE correction causes R_0 to converge considerably fast to the CBS limits. Therefore, adding bond functions in the calculations not only extremely improve the potential energy minima ε but also simultaneously promote the R_0 values. The R_0 values for the vertex Ar + F—CF_3 configuration at the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ levels without BSSE correction were much higher than expected; this might result from the aug-cc-pVDZ basis set being insufficient. To sum up, for the face Ar + F_3C—F and vertex Ar + F—CF_3 orientations, potential energy minima ε and R_0 are better with the bond functions than without, and are closer to their CBS limits.

The influences of bond function positions between the Ar atom and the CF_4 molecule were also studied and the results are shown in Figure 4. All calculations were performed using BSSE correction at each R_0 value determined from individual model chemistry potential energy curves and the bond functions are collinear with Ar—C. It shows the calculated intermolecular potential energy as a function of the distance between bond functions and the Ar—C midpoint. The arrows in the figure indicate the positions which are the lowest points of individual model chemistry potential energy curves. From our calculations at both MP2 and CCSD(T) levels of theory, the optimised bond function positions for the basis sets aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ are about 0.4, 0.5 and 0.3 Å, respectively, away from the Ar—C midpoint tilted towards the Ar atom for the face Ar + F_3C—F configuration; 0.4, 0 and 0.3 Å, respectively,

for the vertex Ar + F—CF_3 configuration. As we expected, optimising the positions of bond functions enables Ar—CF_4 intermolecular interaction potential energy to decrease, especially at the aug-cc-pVDZ level. But the effect is not apparent at the aug-cc-pVTZ and aug-cc-pVQZ levels. Therefore, the dependence of bond function locations on the Ar—CF_4 intermolecular potential energy is significant at the aug-cc-pVDZ level and the bond functions should carefully be placed near the optimal positions for accurate potential energy minima ε values. As shown in Figure 4, the optimisation of bond function positions would cause MP2/bf-aug-cc-pVDZ intermolecular potential energy to be close to the MP2/bf-aug-cc-pVTZ intermolecular potential energy. There are cusps in Figure 4(b); this phenomenon may be the interference of basis functions since bond functions are within collinear C—F atoms. It is plausible to say that the optimal position of bond functions might be the strongest interaction site in van der Waals complexes. In other words, a van der Waals system with bond functions placed at the optimal position would possess the lowest intermolecular interaction energy.

3.3 Two simple approximation methods for the intermolecular interaction energy at the CCSD(T) level

Optimisation of the potential energy minima R_0 at the CSSD(T) level with basis sets of quality higher than that of aug-cc-pVTZ and subsequently extrapolating them to their CBS limits is very time-consuming. Consequently, several approximation methods have been developed to achieve similar results but with reduced computational resources and time. We compared two general approximation methods that are widely used; the first is discussed below [35]. The potential energy minima ε and R_0 for two Ar + CF_4 orientations were determined at the MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, MP2/bf-aug-cc-pVTZ and CCSD(T)/bf-aug-cc-pVTZ levels. In order to evaluate the well depth at the CBS limit for both orientations, additional calculations at the MP2 and CCSD(T) levels were performed with the aug-cc-pVDZ and aug-cc-pVQZ basis sets. For simplicity, the R_0 values used in the two aug-cc-pVDZ and aug-cc-pVQZ basis-set calculations were the same as those of aug-cc-pVTZ. As shown in Table 4, the calculations for the aug-cc-pVDZ and aug-cc-pVQZ basis sets were performed at individual R_0 values determined from these four above-mentioned model chemistries and thereafter extrapolated them to their CBS limits. All of the calculated potential energy minima and fitted CBS limit values in Table 4 are similar to the corresponding values in Table 3, the largest differences not exceeding 0.03 kcal/mol for those calculated with the aug-cc-pVQZ basis set and estimated CBS limit values. The CBS values fitted by MP2/bf-aug-cc-pVXZ and CCSD(T)/bf-aug-cc-pVXZ (where X = D, T, Q, respectively) are similar to CC-CBS values, showing that adding the bond functions to the MP2 and CCSD(T) calculations is reasonable for this approximation method. Again, for all three basis sets, the potential energy minima determined with the bond functions are closer to the CBS limits than those determined without the bond functions. At both configurations with BSSE correction, the potential energy minima at the MP2/bf-aug-cc-pVTZ and CCSD(T)/bf-aug-cc-pVDZ levels can approach those at the CCSD(T)/aug-cc-pVQZ level and CBS limit, respectively.

The other approximation is based on the focal-point method [36,40,43–45]. This method developed from Allen and co-workers [43–45] has been used to estimate

Table 4. Energy and geometry of MP2 and CCSD(T) van der Waals minima using the approximate method with and without BSSE correction, and with and without bond functions[a].

Theory	BSSE	R_0	cc-pVDZ	cc-pVTZ	cc-pVQZ	CBS(T,Q)
Ar + F_3C—F potential curve						
MP2	No corr.	3.712	−0.716	−0.703	−0.644	−0.601
	Corr.	3.813	−0.318	−0.462	−0.517	−0.557
CCSD(T)	No corr.	3.709	−0.761	−0.719	−0.650	−0.599
	Corr.	3.810	−0.307	−0.470	−0.532	−0.577
MP2-bf	Corr.	3.769	−0.522	−0.534	−0.546	−0.554
CCSD(T)-bf	Corr.	3.757	−0.567	−0.563	−0.567	−0.570
Ar + F—CF_3 potential curve						
MP2	No corr.	4.632	−0.420	−0.401	−0.354	−0.319
	Corr.	4.734	−0.179	−0.251	−0.274	−0.291
CCSD(T)	No corr.	4.630	−0.442	−0.411	−0.354	−0.313
	Corr.	4.732	−0.175	−0.256	−0.282	−0.301
MP2-bf	Corr.	4.695	−0.285	−0.286	−0.291	−0.295
CCSD(T)-bf	Corr.	4.684	−0.311	−0.302	−0.303	−0.303

[a] Energies are given in kcal/mol, and Ar—C distance (R_0) values are given in Å. The calculations were performed at individual R_0 values determined from the MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, MP2/bf-aug-cc-PVTZ and CCSD(T)/bf-aug-cc-PVDZ potential energy curves. R_0 values are from Table 3. cc-pVXZ (X = D, T, Q) refers to Dunning's aug-cc-pVXZ (X = D, T, Q) basis sets. CBS represents the complete basis-set limit.

Table 5. Energy and geometry of CCSD(T) van der Waals minima using the focal-point method with and without BSSE correction[a].

BSSE		cc-pVDZ	fp-cc-pVTZ	fp-cc-pVQZ	fp-cc-pV5Z	fp-CBS(T,Q)	fp-CBS(Q,5)
Ar + F$_3$C—F potential curve							
No corr.	R_0	3.689	3.701	3.709	3.716	3.715	3.723
	ε	−0.761	−0.749	−0.690	−0.664	−0.646	−0.638
Corr.	R_0	3.959	3.823	3.781	3.767	3.750	3.752
	ε	−0.331	−0.455	−0.512	−0.532	−0.554	−0.553
Ar + F—CF$_3$ potential curve							
No corr.	R_0	4.685	4.630	4.650	4.655	4.665	4.660
	ε	−0.446	−0.424	−0.377	−0.358	−0.342	−0.338
Corr.	R_0	4.860	4.746	4.715	4.699	4.692	4.682
	ε	−0.186	−0.248	−0.272	−0.284	−0.290	−0.296

[a] Well depths (ε) are given in kcal/mol, and Ar—C distances (R_0) are given in Å. The CCSD(T)/aug-cc-pVDZ values and related MP2 data used in the focal-point method are from Table 3. cc-pVXZ (X = D, T, Q, 5) refers to Dunning's aug-cc-pVXZ (X = D, T, Q, 5) basis sets. CBS represents complete basis-set limit.

CCSD(T) energies with the basis sets higher than aug-cc-pVDZ. The concept of the focal-point method is that the energy differences between the MP2 and CCSD(T) levels are independent of the basis sets. We prefix 'fp-' to the focal-point CCSD(T) energies as fp-CCSD(T) hereafter. The differences between the MP2 and CCSD(T) energies are calculated with a smaller basis set (e.g. aug-cc-pVDZ) for the potential energy surfaces, and those differences were used to estimate the CCSD(T) energies with larger basis sets (e.g. aug-cc-pVTZ and aug-cc-pVQZ) according to the MP2 calculations. That is to say, the interaction energy of fp-CCSD(T)/aug-cc-pVTZ = CCSD(T)/aug-cc-pVDZ + MP2/aug-cc-pVTZ − MP2/aug-cc-pVDZ, fp-CCSD(T)/aug-cc-pVQZ = fp-CCSD(T)/aug-cc-pVTZ + MP2/aug-cc-pVQZ − MP2/aug-cc-pVTZ and so forth. The results from the focal-point method are listed in Table 5. As shown in the table, all the results are close to the corresponding results listed in Table 3; the largest differences of ε and R_0 values are below 0.05 kcal/mol and 0.03 Å, respectively. Thus, the CBS limit values derived from the focal-point method are in agreement with the optimised data. Hence, the focal-point approximation method is a convenient way to determine the Ar + CF_4 potential energy curves without the loss of accuracy.

Table 6. Parameters of the analytic Ar—CF_4 pairwise Buckingham potentials[a].

System	Pair	A	B	C
I	Ar—C	57282.6	3.43606	−185.003
	Ar—F	183,815	4.09467	−517.44
II	Ar—C	106,730	3.65065	−215.022
	Ar—F	176,892	4.10142	−544.761
III	Ar—C	85821.5	3.51857	−250.065
	Ar—F	238,115	4.18777	−560.755

[a] The parameters for systems I, II and III were determined by fitting the CCSD(T)/aug-cc-pVTZ, MP2/CBS and CCSD(T)/bf-aug-cc-pVDZ potential energy curves, respectively.

3.4 Analytic intermolecular potential energy surfaces

It is crucial to obtain accurate analytic intermolecular potential energy surfaces determined from *ab initio* molecular orbital theory in molecular dynamics simulations such as rare gas–organic surface collisions [17]. In this work, electronic structure data at the CCSD(T)/aug-cc-pVTZ, MP2/CBS and CCSD(T)/bf-aug-cc-pVDZ levels, respectively, were used to derive the Ar—CF_4 pairwise analytic potential energy curves [35,36]. The analytic potential energy surfaces are written as a sum of two-body interactions, where these two-body potentials are expressed as a Buckingham potential of the form

$$V_{ij} = A\exp(-Br_{ij}) + C/r_{ij}^6. \quad (2)$$

The potential energy surfaces of the two Ar + CF_4 configurations were fitted simultaneously with a nonlinear least-squares procedure. The fitted parameters are listed in Table 6, and the comparison of ε and R_0 values of *ab initio* and analytic potential is shown in Table 7. As shown in Figure 5, the two-body Buckingham potentials given by Equation (2) are in good agreement with the *ab initio* data in all levels of theory (MP2/CBS level-fitted potential

Table 7. Comparison of *ab initio* and analytic energy and geometry for the Ar—CF_4 van der Waals minima[a].

System		Face	Vertex
I	ε	−0.467 (−0.470)	−0.249 (−0.256)
	R_0	3.816 (3.810)	4.736 (4.732)
II	ε	−0.557 (−0.561)	−0.287 (−0.292)
	R_0	3.742 (3.740)	4.679 (4.680)
II	ε	−0.559 (−0.567)	−0.300 (−0.311)
	R_0	3.767 (3.762)	4.681 (4.688)

[a] Systems I, II and III represent the CCSD(T)/aug-cc-pVTZ, MP2/CBS and CCSD(T)/bf-aug-cc-pVDZ potential energy curves, respectively. Values in parentheses are the corresponding *ab initio* data. Well depths (ε) are given in kcal/mol, and Ar—C distances (R_0) are given in Å.

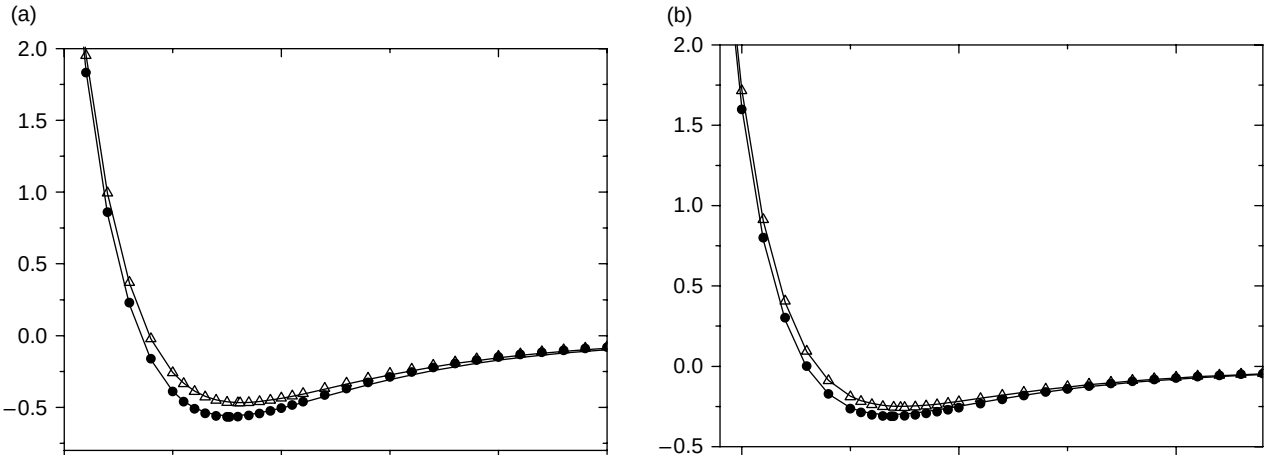

Figure 5. (a) Comparison of *ab initio* and analytic intermolecular potential energy curves for face Ar + F_3C—F. (b) Comparison of *ab initio* and analytic intermolecular potential energy curves for vertex Ar + F—CF_3. Calculated intermolecular potential energy (in kcal/mol) as a function of the Ar—C distance (in Å). All calculations include BSSE correction. The open triangles denote the CCSD(T)/aug-cc-pVTZ potentials and the filled circles denote the CCSD(T)/bf-aug-cc-pVDZ potentials. The corresponding fitted analytic values are shown as solid lines.

energy curves were not shown in the figure for clarity). For the Ar + F_3C—F and Ar + F—CF_3 potential energy curves, the maximum difference in energy between the fitted analytic and *ab initio* ε values is 0.011 kcal/mol, and the R_0 values estimated by the analytic potential energy surfaces are within 0.007 Å of the *ab initio* calculations in all levels of theory.

4. Conclusions

The potential energy surfaces for two Ar + CF_4 orientations were calculated using the MP2 and CCSD(T) theories and several basis sets from aug-cc-pVDZ to aug-cc-pV5Z. The influence of the number of basis functions of basis sets, BSSE and bond functions on the *ab initio* intermolecular interaction energies is significant. The potential energy minima ε and R_0 values determined from the MP2 calculations are similar to the corresponding CCSD(T) results. Adding the bond functions to the MP2 theory improves resulting values of the potential energy minima and the distance between the Ar atom and the CF_4 molecule. Calculation at the MP2/bf-aug-cc-pVTZ level with BSSE corrections may afford deeper ε than those at the CCSD(T)/aug-cc-pVQZ level; however, it is suggested that the MP2/bf-aug-cc-pVQZ level of theory provides more accurate and reliable results for both Ar + CF_4 configurations. Furthermore, the R_0 values determined at the MP2/bf-aug-cc-pVQZ level with BSSE correction are closer to the CBS limits than those determined at the CCSD(T)/aug-cc-pVQZ level. Optimisation of the bond function position between the Ar atom and the CF_4 molecule affords more accurate potential energy minima ε and R_0 values. At smaller basis sets such as aug-cc-pVDZ, the bond functions would probably be placed closer to the optimal positions for accurate potential energy minima. The positions of the bond functions are near the midpoint between the Ar and C atoms, slightly tilted towards the Ar atom. At the CCSD(T)/bf-aug-cc-pVDZ level with BSSE correction, the best potential energy minima ε and R_0 values are obtained, which approach CC-CBS values. Therefore, even when high-level CCSD(T) theory and the large aug-cc-pVQZ basis set are used, adding bond functions to the calculations is suggested for accurate intermolecular interaction potentials. Calculations with bond functions are suitable to evaluate the intermolecular interaction potentials between the Ar rare gas and the non-polar CF_4 molecule; moreover, it saves a great amount of computational resources and time required to acquire CBS estimates at the CCSD(T) level. The attractive region of the potential energy surfaces dominated by dispersion interactions could be easily enhanced to the extent of the CBS limit values if bond functions were included in the *ab initio* calculations. Analytic potential energy surfaces were derived to fit the *ab initio* potential with a sum of Buckingham two-body potential terms. The analytic potentials are in good agreement with the *ab initio* calculations.

Acknowledgements

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References

[1] V. Chechik and R.M. Crooks, *Dendrimer-encapsulated Pd nanoparticles as fluorous phase-soluble catalysts*, J. Am. Chem. Soc. 122(6) (2000), pp. 1243–1244.

[2] U. Gross, G. Papke, and S. Rüdiger, *Fluorocarbons as blood substitutes: Critical solution temperatures of some perfluorocarbons and their mixtures*, J. Fluor. Chem. 61(1–2) (1993), pp. 11–16.

[3] S.R. Cohen, R. Naaman, and J. Sagiv, *Translational energy transfer from molecules and atoms to adsorbed organic monolayers of long-chain amphiphiles*, Phys. Rev. Lett. 58(12) (1987), p. 1208.

[4] M.R. Morris, D.E. Riederer, Jr, B.E. Winger, R.G. Cooks, T. Ast, and C.E.D. Chidsey, *Ion/surface collisions at functionalized self-assembled monolayer surfaces*, Int. J. Mass Spectrom. Ion Process. 122 (1992), pp. 181–217.

[5] J. Laskin and J.H. Futrell, *Energy transfer in collisions of peptide ions with surfaces*, J. Chem. Phys. 119(6) (2003), pp. 3413–3420.

[6] A.L. McCormack, A. Somogyi, A.R. Dongre, and V.H. Wysocki, *Fragmentation of protonated peptides: Surface-induced dissociation in conjunction with a quantum mechanical approach*, Anal. Chem. 65(20) (1993), pp. 2859–2872.

[7] D.J. Garton, T.K. Minton, M. Alagia, N. Balucani, P. Casavecchia, and G.G. Volpi, *Reactive scattering of ground-state and electronically excited oxygen atoms on a liquid hydrocarbon surface*, Faraday Discuss. 108 (1997), pp. 387–399.

[8] O.A. Mazyar, H. Xie, and W.L. Hase, *Nonequilibrium energy dissipation at the interface of sliding model hydroxylated alpha-alumina surfaces*, J. Chem. Phys. 122(9) (2005), pp. 094713–094724.

[9] S.F. Shuler, G.M. Davis, and J.R. Morris, *Energy transfer in rare gas collisions with hydroxyl- and methyl-terminated self-assembled monolayers*, J. Chem. Phys. 116(21) (2002), pp. 9147–9150.

[10] J.R. Morris, W.A. Alexander, and D. Troya, *Theoretical study of the effect of surface density on the dynamics of Ar + alkanethiolate self-assembled monolayer collisions??AU – Day, B. Scott*, J. Phys. Chem. A 110(4) (2005), pp. 1319–1326.

[11] M.E. Saecker, S.T.G. Daniel, V. Kowalski, M.E. King, and G.M. Nathanson, *Molecular beam scattering from liquid surfaces*, Science 252 (1991), pp. 1421–1424.

[12] M.E. King, G.M. Nathanson, M. Hanning-Lee, and T.K. Minton, *Probing the microscopic corrugation of liquid surfaces with gas–liquid collisions*, Phys. Rev. Lett. 70(7) (1993), p. 1026.

[13] K.D. Gibson, N. Isa, and S.J. Sibener, *Experiments and simulations of Ar scattering from an ordered 1-decanethiol – Au(111) monolayer*, J. Chem. Phys. 119(24) (2003), pp. 13083–13095.

[14] B.S. Day and J.R. Morris, *Packing density and structure effects on energy-transfer dynamics in argon collisions with organic monolayers*, J. Chem. Phys. 122(23) (2005), pp. 234714–234723.

[15] B.S. Day, J.R. Morris, and D. Troya, *Classical trajectory study of collisions of Ar with alkanethiolate self-assembled monolayers: Potential-energy surface effects on dynamics*, J. Chem. Phys. 122(21) (2005), pp. 214712–214723.

[16] J.N. Murrell, S. Carter, S. Frantos, P. Huxley, and A.J.C. Varandas, *Molecular Potential Energy Functions*, John Wiley & Sons, New York, 1984.

[17] S.A. Vázquez, J.R. Morris, A. Rahaman, O.A. Mazyar, G. Vayner, S.V. Addepalli, W.L. Hase, and E. Martínez-Núñez, *Inelastic scattering dynamics of Ar from a perfluorinated self-assembled monolayer surface AU – Vazquez, Saulo A*, J. Phys. Chem. A 111(49) (2007), pp. 12785–12794.

[18] S. Tsuzuki, T. Uchimaru, and K. Tanabe, *Intermolecular interaction potentials of methane and ethylene dimers calculated with the Møller–Plesset, coupled cluster and density functional methods*, Chem. Phys. Lett. 287(1–2) (1998), pp. 202–208.

[19] A.D. Buckingham, P.W. Fowler, and J.M. Hutson, *Theoretical studies of van der Waals molecules and intermolecular forces*, Chem. Rev. 88(6) (1988), pp. 963–988.

[20] J. Sponer and P. Hobza, *MP2 and CCSD(T) study on hydrogen bonding, aromatic stacking and nonaromatic stacking*, Chem. Phys. Lett. 267(3–4) (1997), pp. 263–270.

[21] S. Tsuzuki, T. Uchimaru, and K. Tanabe, *Basis set effects on the intermolecular interaction of hydrocarbon molecules obtained by an* ab initio *molecular orbital method: Evaluation of dispersion energy*, J. Mol. Struct. Theochem. 307 (1994), pp. 107–118.

[22] S. Tsuzuki and K. Tanabe, *Basis set effects on the intermolecular interaction energies of methane dimers obtained by the Møller–Plesset perturbation theory calculation*, J. Phys. Chem. 95(6) (1991), pp. 2272–2278.

[23] F.-M. Tao, *Bond functions, basis set superposition errors and other practical issues with* ab initio *calculations of intermolecular potentials*, Int. Rev. Phys. Chem. 20(4) (2001), pp. 617–643.

[24] F.-M. Tao, Ab initio *calculation of the interaction potential for the krypton dimer: The use of bond function basis sets*, J. Chem. Phys. 111(6) (1999), pp. 2407–2413.

[25] F.-M. Tao, Z. Li, and Y.-K. Pan, *An accurate* ab initio *potential energy surface of He—H_2O*, Chem. Phys. Lett. 255(1–3) (1996), pp. 179–186.

[26] T. Fu-Ming, *Notes on the Use of Bond Functions for* ab initio *Intermolecular Energy Calculations*, Vol. 367, Elsevier Science, Fullerton, CA, 1996, pp. 55–57.

[27] F.-M. Tao, *The counterpoise method and bond functions in molecular dissociation energy calculations*, Chem. Phys. Letters 206(5–6) (1993), pp. 560–564.

[28] F.-M. Tao, *The use of midbond functions for* ab initio *calculations of the asymmetric potentials of He—Ne and He—Ar*, J. Chem. Phys. 98(4) (1993), pp. 3049–3059.

[29] T. Fu-Ming, *On the use of bond functions in molecular calculations*, J. Chem. Phys. 98(3) (1993), pp. 2481–2483.

[30] F.-M. Tao and Y.-K. Pan, Ab initio *potential energy curves and binding energies of Ar_2 and Mg_2*, Mol. Phys. Int. J. Interface Chem. Phys. 81(3) (1994), pp. 507–518.

[31] T. Fu-Ming and K. William, *Accurate* ab initio *potential energy surfaces of Ar—HF, Ar—H_2O, and Ar—NH_3*, J. Chem. Phys. 101(2) (1994), pp. 1129–1145.

[32] T. Fu-Ming and K. William, Ab initio *potential energy surface for the HCl dimer*, J. Chem. Phys. 103(3) (1995), pp. 950–956.

[33] T. Fu-Ming and W. Klemperer, Ab initio *search for the equilibrium structure of the ammonia dimer*, J. Chem. Phys. 99(8) (1993), pp. 5976–5982.

[34] D.M. Hirst, *Potential Energy Surfaces: Molecular Structure and Reaction Dynamics*, Taylor and Francis, London, 1985.

[35] G. Vayner, Y. Alexeev, J. Wang, T.L. Windus, and W.L. Hase, Ab Initio *and analytic intermolecular potentials for Ar—CF_4*, J. Phys. Chem. A 110(9) (2006), pp. 3174–3178.

[36] W.A. Alexander and D. Troya, *Theoretical study of the Ar-, Kr-, and Xe-CH4, -CF4 intermolecular potential-energy surfaces*, J. Phys. Chem. A 110(37) (2006), pp. 10834–10843.

[37] A.K. Wilson, D.E. Woon, K.A. Peterson, and T.H. Dunning, *Gaussian basis sets for use in correlated molecular calculations. IX. The atoms gallium through krypton*, J. Chem. Phys. 110(16) (1999), pp. 7667–7676.

[38] S.F. Boys and F. Bernardi, *The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors*, Mol. Phys. 19(4) (1970), pp. 553–566.

[39] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, *Gaussian 03*, *Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.

[40] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A.K. Wilson, *Basis-set convergence in correlated*

calculations on Ne, N_2, and H_2O, Chem. Phys. Lett. 286(3–4) (1998), pp. 243–252.

[41] K.A. Peterson, D.E. Woon, and J.T.H. Dunning, *Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the $H + H_2 \rightarrow H_2 + H$ reaction*, J. Chem. Phys. 100(10) (1994), pp. 7410–7415.

[42] S. Tsuzuki, T. Uchimaru, M. Mikami, and S. Urata, *Magnitude and orientation dependence of intermolecular interaction between perfluoroalkanes: High level* ab initio *calculations of CF_4 and C_2F_6 dimers*, J. Chem. Phys. 116(8) (2002), pp. 3309–3315.

[43] G.C. Attila, D.A. Wesley, and F.S. Henry, III, *In pursuit of the* ab initio *limit for conformational energy prototypes*, J. Chem. Phys. 108(23) (1998), pp. 9751–9764.

[44] N.L. Allinger, J.T. Fermann, W.D. Allen, and H.F. Schaefer III, *The torsional conformations of butane: Definitive energetics from* ab initio *methods*, J. Chem. Phys. 106(12) (1997), pp. 5143–5150.

[45] L.L.E. Allan and D.A. Wesley, *The heat of formation of NCO*, J. Chem. Phys. 99(6) (1993), pp. 4638–4650.