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Grigoriy Vayner, *Pacific Northwest National Laboratory*
Yuri Alexeev, *Texas Tech University*
Jiangping Wang, *Wayne State University*
Theresa L. Windus, *Texas Tech University*
William L. Hase, *Pacific Northwest National Laboratory*

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Grigoriy Vayner,[‡] Yuri Alexeev,[§] Jiangping Wang,[#] Theresa L. Windus,[§] and William L. Hase*,[‡]

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, and Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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Ab initio calculations at the CCSD(T) level of theory were performed to characterize the Ar + CF_4 intermolecular potential. Potential energy curves were calculated with the aug-cc-pVTZ basis set, and with and without a correction for basis set superposition error (BSSE). Additional calculations were performed with other correlation consistent basis sets to extrapolate the Ar−CF_4 potential energy minimum to the complete basis set (CBS) limit. Both the size of the basis set and BSSE have substantial effects on the Ar + CF_4 potential. Calculations with the aug-cc-pVTZ basis set, and with a BSSE correction, appear to give a good representation of the BSSE corrected potential at the CBS limit. In addition, MP2 theory is found to give potential energies in very good agreement with those determined by the much higher level CCSD(T) theory. Two model analytic potential energy functions were determined for Ar + CF_4. One is a fit to the aug-cc-pVTZ calculations with a BSSE correction. The second was derived by fitting an average BSSE corrected potential, which is an average of the CCSD(T)/aug-cc-pVTZ potentials with and without a BSSE correction. These analytic functions are written as a sum of two-body potentials and excellent fits to the ab initio potentials are obtained by representing each two-body interaction as a Buckingham potential.

I. Introduction

There is considerable interest in studying the dynamics of energy transfer in collisions of projectiles with hydrocarbon surfaces.[1−9] The projectiles that have been investigated include rare gas atoms,[1,5−9] O(^{3}P) atoms,[4,10,11] and a number of different ions,[2,3,12,13] including protonated peptides. The collision energies studied for the atoms range from thermal (i.e., 300 K) to 5 eV, whereas much higher collision energies of 5−150 eV have been considered for the ions. Understanding the efficiency of this energy transfer is of fundamental as well as practical interest. Energy transfer to hydrocarbon surfaces is important for the degradation of polymer surfaces on spacecraft in low-earth orbit (LEO),[4] for controlling friction in mechanical devices,[14] and for achieving efficient fragmentation of peptides in surface-induced dissociation (SID).[2,3]

Self-assembled monolayers (SAMs) have been used to investigate how the structure of the hydrocarbon surface affects the efficiency of collisional energy transfer.[7,8] For collisions of both rare gas atoms and protonated peptides, fluorinated alkanethiolate SAMs (i.e., F-SAM) absorb energy less efficiently than do their hydrogenated counterparts. This has been attributed to a mass effect (i.e., F versus H) and/or different degrees of stiffness of the F-SAM and H-SAM surfaces.[1,2]

Classical trajectory simulations, utilizing accurate potential energy functions, give energy distributions in excellent agreement with experiment for both rare gas atom[6,9] and protonated peptide[12] projectiles colliding with H-SAMs. Because the trajectories give an atomic-level description of the gas−surface collision, they also provide an elementary, microscopic understanding of the energy transfer dynamics. This information is needed to develop accurate models for energy transfer in gas−surface collisions.

Experiments have studied the efficiency of energy transfer in Ar-atom collisions with both H-SAM and F-SAM alkanethiolate surfaces.[7,15−18] Trajectory simulations give an excellent representation of the experimental energy distribution for Ar-atoms scattered off the H-SAM surface.[16−19] However, similar simulations have not been performed for the Ar + F-SAM system, because an accurate intermolecular potential has not been developed for Ar interacting with the F-SAM. In the work presented here an ab initio potential is calculated for Ar + CF_4 to model the potentials for Ar interacting with the carbon and fluorine atoms of the F-SAM. An important component of this research is establishing the level of theory needed to calculate an accurate Ar + CF_4 intermolecular potential.

II. Electronic Structure Calculations

A. Procedure. The quantum mechanical calculations were performed using the MOLPRO package,[20] with preliminary calculations performed with NWChem.[21] Energies were computed with and without basis set superposition error (BSSE) correction, using the standard counterpoise method of Boys and Bernardi.[22] The core electrons were excluded from the electron correlation in the MP2 and coupled cluster calculations. CCSD(T) total energies were extrapolated to the complete basis set (CBS) limit. The formula used is that proposed by Peterson et al.[23] in the form of a mixed exponential/Gaussian function

$$E(n) = E_{CBS} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (1)$$

where $n = 2$, 3, and 4 represent the DZ, TZ, and QZ energies. In the calculations of the Ar + CF_4 intermolecular potential, CF_4 is held fixed in its equilibrium geometry.

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[‡] Texas Tech University.
[§] Pacific Northwest National Laboratory.
[#] Wayne State University.

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TABLE 1: CCSD(T) Potential Energy Minima with Different Basis Sets, and with and without BSSE Correction[a]

BSSE	R_o (Å)	cc-pVDZ[b]	cc-pVTZ[b]	cc-pVQZ[b]	CBS
		Ar + F_3C−F Potential Curve			
no corr	3.717	−0.756	−0.714	−0.645	−0.596
corrn	3.818	−0.308	−0.466	−0.527	−0.558
		Ar + F−CF_3 Potential Curve			
no corr	4.630	−0.469	−0.411	−0.350	−0.307
corrn	4.949	−0.174	−0.253	−0.279	−0.295

[a] The calculations are performed at the R_o values listed above, determined from the CCSD(T)/aug-cc-pVTZ potential energy curves. Values for the potential energy minima are given in kcal/mol. R_o is the distance between the Ar and C atoms. [b] The augumented (aug) basis sets were used.

B. Results. *1. Potential Energy Minima.* Intermolecular potential energy curves and their minima were studied for two orientations of Ar−CF_4. Both orientations have C_{3v} symmetry with the Ar-atom collinear with a C−F bond. For one curve Ar is approaching a CF_3 face of CF_4 and for the other curve Ar approaches a F-atom. These two configurations are identified as Ar + F_3C−F and Ar + F−CF_3. The positions and depths of the potential energy minima for these two curves were determined at the CCSD(T)/aug-cc-pVTZ level of theory. Calculations were performed that did and did not include a correction for basis set superposition error (BSSE). The Ar−C separations at the potential energy minima, denoted by R_o, and the depths of the potential minima are listed in Table 1. Including the BSSE correction decreases the depth of the potential energy minima and shifts them to greater Ar−C separations.

Additional CCSD(T) calculations, at the aug-cc-pVTZ R_o values, were performed with the aug-cc-pVDZ and aug-cc-pVQZ basis sets for both the Ar + F_3C−F and Ar + F−CF_3 systems to establish the CBS limit for the well depths and to determine the sensitivity of the well depths to the size of the basis set. The results of these calculations are also given in Table 1. Increasing the size of the basis set from aug-cc-pVTZ to aug-cc-pVQZ gives potential minima which are 0.07 and 0.06 kcal/mol shallower for the two curves without a BSSE correction and well depths 0.06 and 0.03 kcal/mol deeper for the two curves with the correction. These are small changes.

The aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ energies were fit with eq 1 to determine the CBS limit for the minima of the Ar + F_3C−F and Ar + F−CF_3 CCSD(T)/aug-cc-VTZ potential energy curves. As shown in Table 1, the resulting CBS values of the potential energy minima are similar for the curves with and without BSSE. For the calculations without BSSE correction, the CBS minima for the two curves are 0.12 and 0.10 kcal/mol shallower than their aug-cc-pVTZ values. However, with the BSSE correction, the differences are smaller and the CBS potential energy minima are 0.09 and 0.04 kcal/mol deeper. The suggestion from this comparison is that the aug-cc-pVTZ potential energy curves, with a BSSE correction, provide a useful model for the CBS potential energy curves with BSSE correction. It is also of interest that the average of the aug-cc-pVTZ potential energy minimum with and without a BSSE correction is a better approximation to the CBS minimum for both the Ar + F_3C−F and Ar + F−CF_3 potential curves. This average aug-cc-pVTZ minimum energy is −0.59 and −0.33 kcal/mol for Ar + F_3C−F and Ar + F−CF_3, respectively. The average of aug-cc-pVTZ potential energy curves, with and without BSSE correction, may provide a more accurate potential energy curve than the aug-cc-pVTZ curve with BSSE correction. Such a result would not be surprising, because the aug-cc-pVTZ basis set is incomplete with respect to the CBS limit and for such a basis set the counterpoise method may overcorrect the BSSE.[24,25]

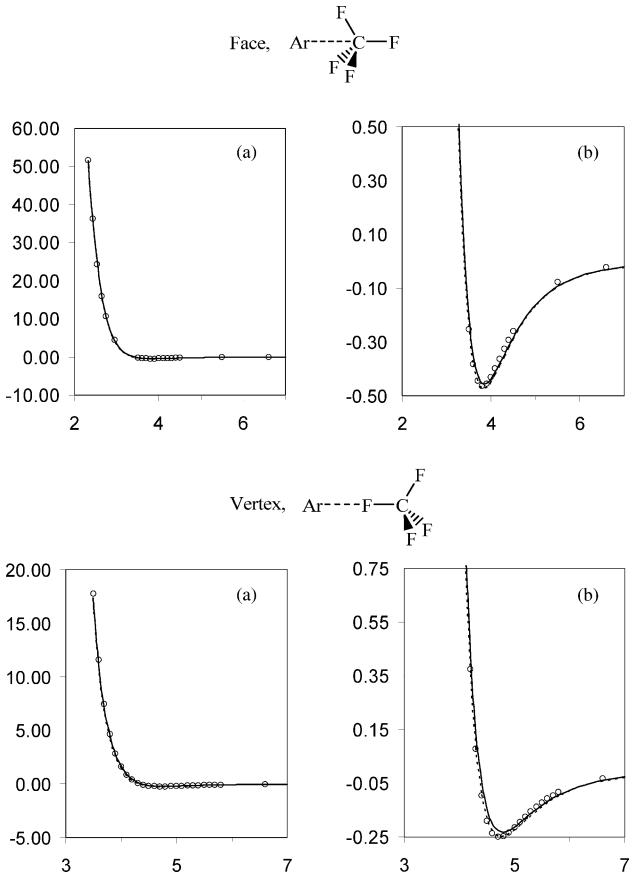

Figure 1. Ar + CF_4 potential energy curves for the face and vertex orientations. The points give the CCSD(T)/aug-cc-pVTZ potential with BSSE correction. The lines are fits as described in the text. (a) Complete high and low energy potential energy curve. The solid line is the fit by eq 2 and the fit by eq 3 is indistinguishable on this plot. (b) Potential energy curve for only the low energies. The solid and dashed lines are the fits by eqs 2 and 3, respectively. Energy is in kcal/mol. The *x*-axis is the Ar−C distance in angstroms.

2. Ar + F_3C−F and Ar + F−CF_3 Potential Energy Curves. The CCSD(T)/aug-cc-pVTZ potential energy curves with BSSE correction are shown in Figure 1. Potential energy curves which are an average of the CCSD(T)/aug-cc-pVTZ potential energy curves with and without BSSE correction are plotted in Figure 2. These curves are identified as average BSSE corrected. The CCSD(T)/aug-cc-pVTZ energies for the Ar + F_3C−F potential energy curve with and without BSSE correction are compared in Table 2.

The Ar−C separation, R_o, and minimum potential energy, V_o, for the average BSSE corrected potential energy curves are compared with the potential energy curves with BSSE correction in Table 3. The values of V_o for the average BSSE corrected curves are in very good agreement with the CBS values in Table 1.

3. Comparison of MP2 and CCSD(T) Potential Energy Curves. In previous work, MP2 theory[26−28] has been found to give accurate intermolecular potential energy curves. A MP2 calculation requires considerably less computer time than does a CCSD(T) calculation and it is of interest to determine whether MP2 theory gives an accurate intermolecular potential for Ar + CF_4. To make this comparison, potential energy curves for both the Ar + F_3C−F and Ar + F−CF_3 orientations were calculated at the MP2 level of theory using the aug-cc-pVTZ basis set. The MP2 and CCSD(T) potential energy curves for

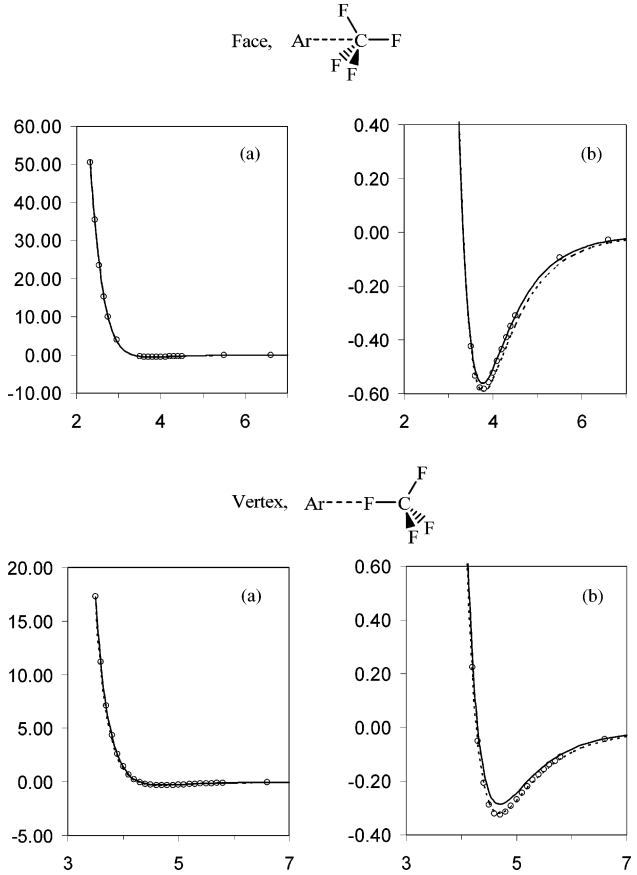

Figure 2. Same as Figure 1, except for the CCSD(T)/aug-cc-pVTZ potential with an average BSSE correction.

TABLE 2: Comparison of Potential Energies with and without BSSE Correction[a]

	MP2		CCSD(T)	
Ar−C[b]	no corr	with corr	no corrn	with corrn
2	146.90	149.98	148.83	152.04
2.11	103.40	106.03	104.79	107.53
2.22	71.67	73.92	72.65	75.00
2.33	48.90	50.83	59.49	51.60
2.43	36.05	35.71	34.54	36.27
2.54	22.45	23.86	22.78	24.24
2.65	14.46	15.65	14.67	15.90
2.75	9.54	10.45	9.58	10.62
2.95	3.56	4.29	3.60	4.36
3.5	−0.58	−0.25	−0.60	−0.25
3.6	−0.67	−0.38	−0.69	−0.38
3.7	−0.70	−0.44	−0.71	−0.45
3.8	−0.69	−0.46	−0.70	−0.46
3.9	−0.65	−0.45	−0.66	−0.46
4.0	−0.60	−0.43	−0.61	−0.43
4.1	−0.55	−0.39	−0.56	−0.40
4.2	−0.50	−0.36	−0.51	−0.36
4.3	−0.45	−0.32	−0.45	−0.33
4.4	−0.40	−0.29	−0.41	−0.29
4.5	−0.36	−0.26	−0.36	−0.26

[a] Energies are in kcal/mol. The aug-cc-pVTZ basis set was used for the calculations. [b] The Ar−C distance is for the face configuration (see Figure 1) and is given in angstroms.

the Ar + F_3C−F orientation are compared in Table 2 and seen to be in good agreement. The MP2 and CCSD(T) values for R_o and V_o are compared in Table 3 for the calculations with BSSE correction. Their potential energy minima are in very good agreement with values for V_o that differ by only 0.01−0.02 kcal/mol and R_o values that differ by less than 0.01 Å. The average error in relative energies between CCSD(T) and MP2 is only 3%. MP2 theory will give an accurate intermolecular potential for Ar + CF_4.

TABLE 3: CCSD(T), MP2, and Fitted Parameters for the Ar−CF_4 Potential Energy Minima[a]

	BSSE corrn		av BSSE corrn	
	R_o	V_o	R_o	V_o
	Ar + F_3C−F Potential Curve			
MP2	3.82	−0.455	3.76	−0.572
CCSD(T)	3.82	−0.466	3.76	−0.584
fit, eq 2[b]	3.85	−0.457	3.76	−0.561
fit, eq 3	3.84	−0.462	3.78	−0.592
	Ar + F−CF_3 Potential Curve			
MP2	4.73	−0.246	4.68	−0.318
CCSD(T)	4.73	−0.253	4.68	−0.325
fit, eq 2[b]	4.78	−0.225	4.70	−0.286
fit, eq 3	4.75	−0.241	4.68	−0.318

[a] The ab initio calculations were performed with the aug-cc-pVTZ basis set. R_o is in angstroms and V_o in kcal/mol. R_o is the Ar−C distance. [b] The fits are to the CCSD(T)/aug-cc-pVTZ potential energy curves.

III. Analytic Intermolecular Potentials

A. Explicit-Atom (EA) Models. To use a potential determined from electronic structure theory in a molecular dynamics (MD) or chemical dynamics (CD) simulation, it is beneficial to have an analytic representation of the potential. In this work two different models were used to fit the two CCSD(T)/aug-cc-pVTZ Ar + CF_4 potential energy curves. For each model, the potential is written as a sum of two-body interactions between Ar and the C and F atoms of CF_4. For one model, these two-body potentials are written as a Buckingham potential, i.e.

$$V = A\exp(-Br) + C/r^6 \tag{2}$$

For the second model, an additional term is added to the two-body interaction to give

$$V = A\exp(-Br) + C/r^6 + \mathrm{D/r}^9 \tag{3}$$

In fitting the parameters for the latter model, the *A*, *B*, and *C* parameters were restricted to physically meaningful values as identified by the fits to eq 2. The Ar + F_3C−F and Ar + F−CF_3 potential energy curves were fit simultaneously with the sum of two-body potentials. Also, the CCSD(T)/aug-cc-pVTZ ab initio calculations both with BSSE correction and with an average BSSE correction were fit by the potential models. The fitting was done by first using a genetic algorithm[29] to determine a range of sets of approximate fitting parameters. Each set was then further refined by a steepest descent algorithm. The refined set that gave the best fit was then selected.

The fits to the ab initio potential energy curves are shown in Figures 1 and 2, with the fitted parameters listed in Table 4. Values for R_o and V_o determined from these fits are compared with the ab initio values in Table 3. As expected, the second model with more parameters gives a better fit to the ab initio curves than does the first model for which the two-body potential in eq 2 has only the Buckingham term. However, the fit with the first model is over all quite good. For the Ar + F_3C−F curves, with BSSE correction and average BSSE correction, the fitted values of V_o are 0.009 and 0.023 kcal/mol different than the ab initio values for the two respective curves. The fitted values of R_o values are 0.03 and less than 0.01 Å different. For the Ar + F−CF_3 curves, the fitted values of V_o are 0.018 and 0.039 kcal/mol different and the fitted values of R_o are 0.05 and 0.02 Å different. Also, as shown by Figures 1 and 2, this

TABLE 4: Parameters for the Explicit-Atom Fitted Potentials[a]

	A	*B*	*C*	*D*
Potential with BSSE Correction				
		Fit with Eq 2		
Ar−C	60723	3.518	−157.6	
Ar−F	85288	3.790	−556.5	
		Fit with Eq 3		
Ar−C	60244	3.531	−146.5	3858.3
Ar−F	89413	3.822	−572.1	211.1
Potential with Average BSSE Correction				
		Fit with Eq 2		
Ar−C	43991	3.387	−280.6	
Ar−F	129442	3.965	−571.8	
		Fit with Eq 3		
Ar−C	45533	3.360	−249.9	598.5
Ar−F	84565	3. 868	−710.4	5159.4

[a] The parameters were determined by fitting the CCSD(T)/aug-cc-pVTZ potential energy curves as described in the text.

model gives good fits to the complete potential curves. For the second model, with the two-body potential in eq 3, the V_o and R_o values are in excellent agreement with the ab initio values, differing by less than 0.012 kcal/mol and 0.02 Å, respectively, for both the Ar + F_3C−F and Ar + F−CF_3 curves. The average absolute deviation between the ab initio energies, within 1 kcal/mol of the potential minimum, and their fit by eq 3 is 0.011 kcal for both the curves with BSSE correction (Figure 1) and the curves with average BSSE correction (Figure 2). For the fit with eq 2, this deviation is 0.019 for the curves with BSSE correction and 0.018 for the curves with average BSSE correction. When eq 2 is used, the average percent deviations for points above 1 kcal/mol are 1.9 and 2.6 for the curves with BSSE correction and average BSSE correction, respectively. The average percent deviations with eq 3 are 5.1 and 5.3 for the curves with BSSE and average BSSE correction.

As shown in Table 4, both eqs 2 and 3 give physically realistic values for the Buckingham *B* and *C* parameters. For the potential with BSSE correction, the *A*, *B*, and *C* parameters change very little when fitting with eq 3 instead of eq 2. There are significant changes in the *A* and *C* parameters for Ar−F when the potential is fit with an average BSSE correction with eq 3 instead of eq 2.

B. United-Atom (UA) Model. To simulate collisions of a projectile with a surface, a many-atom model for the surface is often required. Simulations for such a large model may require a substantial amount of computer time, and thus, there are incentives to develop approaches which reduce the size of the model. The number of atoms required to represent the surface may be reduced by treating the atoms within a functional group, e.g., $-CH_3$ or $-CH_2$, as a united atom (UA). Such potentials are widely used to represent surfaces, interfaces, and liquids.

UA potentials were developed for the $-CF_3$ and $-CF_2-$ groups of a fluorinated alkane by assuming their potentials are the same as that for isotropic CF_4. To calculate a potential energy curve for an isotropic CF_4 interaction from the explicit-atom (EA) potentials, CF_4 is held rigid in its equilibrium geometry and then randomly rotated to calculate an average potential for a specific distance *R* between Ar and the C-atom of CF_4. The potential energy for each of these random orientations is calculated from the explicit-atom two-body potentials in eq 3. Such a UA potential curve was determined for both the explicit-atom model fit to the calculations with BSSE correction and the model fit to the calculations with an average BSSE correction. The averaging over the EA potentials to determine the UA potential is given by

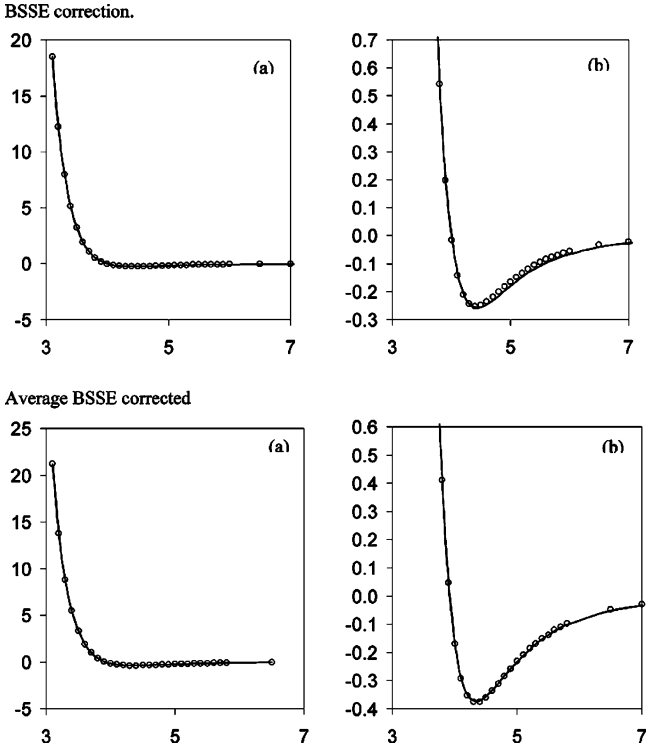

Figure 3. Ar + CF_4 potential energy curves for the united atom model. The circles are the energies averaged over different orientations of CF_4 according to eq 4, and the solid curve is the Buckingham UA potential fit to them. The upper graphs represent the calculations with BSSE correction and the lower graphs represent the average BSSE corrected calculations. (a) Complete high and low energy potential energy curve. (b) Potential energy curve for only the low energies. Energy is in kcal/mol.

$$V^{UA}(R) = \frac{1}{N}\sum_{k=1}^{n}\sum_{i} V_R(r_{i,Ar};\theta_k,\varphi_k,\chi_k) \qquad (4)$$

where $V^{UA}(R)$ is the potential at Ar−C separation *R* with the orientation of CF_4 isotropically averaged to represent a united-atom (UA), *N* is the number of random orientations for the averaging, the *i* identify the C and F atoms of CF_4, $r_{i,Ar}$ is the distance between this i-atom and Ar, θ_k, φ_k, and χ_k are the randomly chosen Euler angles[40] for CF_4, and $V_R(r_{i,Ar};\theta_k,\varphi_k,\chi_k)$ is the two-body potential in eq 3 for the CF_4 random orientation and C−Ar separation *R*. The uncertainty in the average energy for each *R* is less than 0.01 kcal/mol. The resulting two UA potential energy curves are shown in Figure 3. The minimum for the curve with BSSE has a potential of −0.373 kcal/mol at a distance of 4.34 Å. With an average BSSE correction the minimum's potential and distance are −0.253 kcal/mol and 4.44 Å, respectively.

To fit the $V^{UA}(R)$ potential curve, an analytic function is needed to represent the interaction between the CF_4 united-atom (UA) and the Ar-atom. This analytic function is modeled by a two-body Buckingham potential between UA and Ar, given by eq 2. The potential energy parameters derived from the fits are listed in Table 5. Excellent fits to the two $V^{UA}(R)$ potential energy curves were obtained as shown in Figure 3. The parameters for the minima of the fitted curve with BSSE correction are $V_o = -0.373$ kcal/mol and $R_o = 4.34$ Å. For the curve with an average BSSE correction these parameters are −0.258 kcal/mol and 4.43 Å. These fitted parameters for the

TABLE 5: Parameters for the United-Atom Fitted Potentials

potential	*A*	*B*	*C*
with BSSE corr	2653300.	3.777	−2931.4
with av BSSE corr	4185200.	3.873	−3893.5

potential energy minima are in excellent agreement with those given above for the UA potential energy curves.

IV. Summary

Ab initio calculations at the CCSD(T)/aug-cc-pVTZ level of theory were performed to determine an accurate potential energy surface for the Ar + CF_4 intermolecular interaction. Both explicit-atom (EA) and united-atom (UA) analytic functions were derived for this surface by fitting the ab initio potential with a sum of Buckingham two-body potential terms. These model potentials give excellent fits to the ab initio calculations. Both the size of the basis set and basis set superposition error (BSSE) have important effects on the ab initio potential. Ab initio calculations at the lower MP2 level of theory give potential energies in excellent agreement with the CCSD(T) results. That MP2 agrees with CCSD(T) suggests the Ar and CF_4 polarizabilities and the CF_4 multiple moments are well represented by MP2 theory, and it would be of interest to explore this conjecture in future work. The CCSD(T) calculations were extrapolated to the complete basis set (CBS) limit and it is found that the calculations with the aug-cc-pVTZ basis set and with a BSSE correction give a good representation of the CBS potential with a BSSE correction. An average BSSE corrected potential, which is an average of the CCSD(T)/aug-cc-pVTZ potentials calculated with and without BSSE correction, provides an even better fit to the CBS potential. The Ar−CF_4 van der Waals minimum has C_{3v} symmetry, with Ar approaching the backside of CF_3. The CCSD(T)/aug-cc-pVTZ calculations with a BSSE correction give a minimum that has an Ar−C separation $R_o = 3.818$ Å and a well depth $V_o = -0.466$ kcal/mol. The average BSSE corrected CCSD(T)/aug-cc-pVTZ potential gives $R_o = 3.760$ Å and $V_o = -0.584$ kcal/mol. The CBS well-depth is −0.558 and −0.598 kcal/mol, respectively, with and without a BSSE correction. The accuracy of the average BSSE corrected potential may be a concidence, but it is not surprising. The aug-cc-pVTZ basis set is incomplete with respect to the CBS limit. For such a basis set the counterpoise method overcorrects the BSSE.[24,25] Averaging with the curve without a BSSE correction may compensate for this overcorrection.

The Ar + CF_4 EA and UA analytic potentials were developed for a fixed C−F distance. Such models are appropriate when the C−F bonds are not highly excited, which is the case for Ar collisions with 300 K fluorinated hydrocarbon molecules, liquids, and surfaces. Because the nature of the Ar + CF_4 intermolecular potential is expected to depend on the C−F bond length, these EA and UA potentials should be tested before they are used to model Ar collisions with highly excited fluorinated molecules and materials. The Ar + CF_4 ab initio potential is well-described by an EA potential written as a sum of two-body functions. For other intermolecular potentials such an isotropic model is inappropriate.[30]

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