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Abstract

The intermolecular potential energy surface of the CF_4–CF_4 system is explored by means of ab initio molecular orbital calculations at the HF and MP2 level of theory. A number of progressively larger basis sets (up to 6-311+G(3d)) are used in order to evaluate the basis set effect. The HF energy component of the total interaction energy is somewhat affected by the choice of the basis set. The second-order correlation correction $E(2)$ to the interaction energy is greatly changed with the choice of the basis set. The nonbonding parameters of the Lennard–Jones and the Buckingham potential energy functions are fitted to the ab initio MP2/6-31+G(3d) interaction energies for nine different orientations and a total of 130 configurations. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carbon tetrafluoride; Ab initio calculations; Basis set effects; Intermolecular potential

1. Introduction

Ab initio quantum mechanical calculations offer a way to obtain intermolecular potentials of molecules. This approach can be used to extract detailed information of the potential energy surface, which is sometimes difficult or practically impossible by other methods [1]. Nevertheless, the quality of the potential is sensitive to the level of theory used for the calculation of the interaction energies. Also the basis set superposition error (BSSE) has a significant effect on the calculated interaction potential and therefore it should be corrected for [2].

Previous studies have represented the interaction between two CF_4 molecules by a spherically symmetric part arising from the attractive dispersion forces and the short-range repulsive forces, together with an electrostatic octopole–octopole interaction [3]. More recently the Lennard–Jones parameters for some fluorine-substituted methanes, including CF_4, have been obtained using liquid simulations [4] and ab initio calculations [5]. However, a detailed evaluation of the basis set effect on the calculated interaction potential of the CF_4–CF_4 system has not been reported. In this paper, we systematically evaluate the effects that the choice of progressively larger basis sets (up to 6-311+G(3d)) has on the calculated intermolecular potential energy surface of the CF_4 dimer. As CF_4 does not possess permanent dipole moment, the attractive regions on the dimer surface arise from induced dipole interactions. To describe the attractive regions on the potential energy surface properly, electron correlation correction is included

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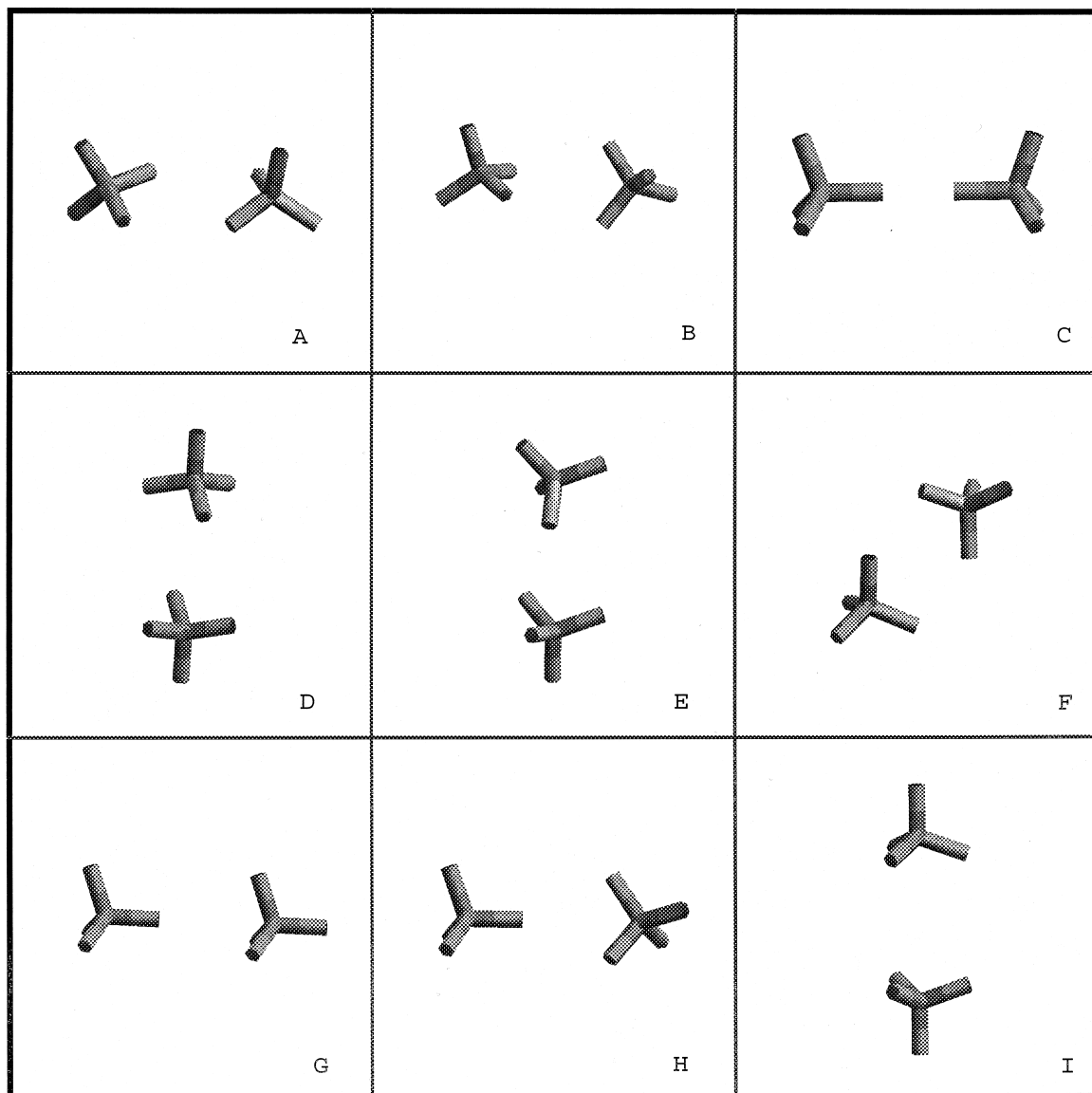*E-mail address:* ruben@super2a.unl.edu (R.D. Parra).

Fig. 1. Nine orientations of the CF_4–CF_4 system considered in this work.

by using the second-order level of Møller–Plesset perturbation theory (MP2).

2. Computational technique

The GAUSSIAN 98 program [6] was used for the molecular orbital calculations. The electron correlation energy was corrected by the MP2 method. It

should be pointed out that, although the MP2 method captures large part of the electron correlation energy, more sophisticated methods can change the calculated interaction energies [7,8]. It is also important to stress that energies of interaction between two closed shell species computed at the MP2 level can turn out to be quite inaccurate [16].

The BSSE was corrected for by the counterpoise procedure [9]. The significance of the BSSE on
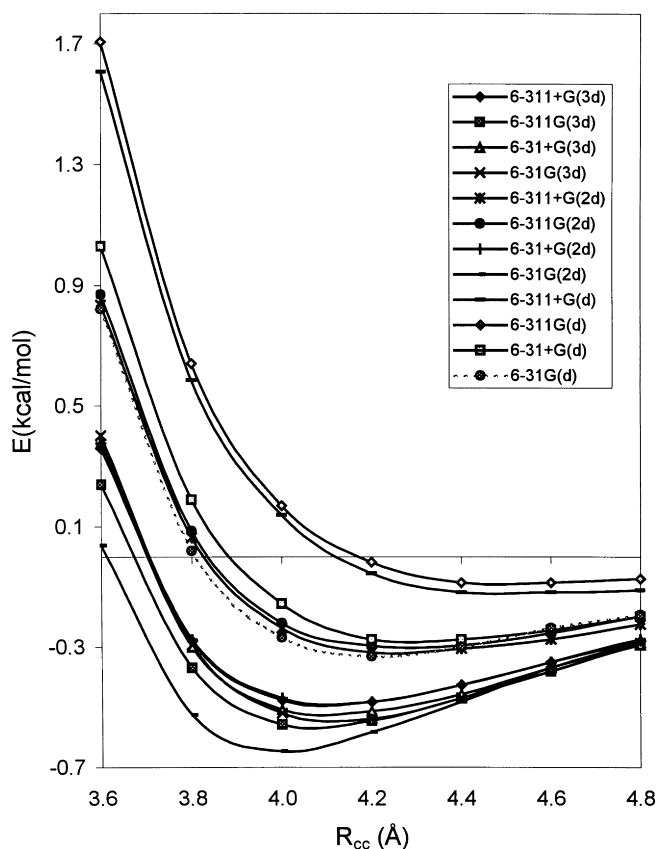
Fig. 2. Basis set effect on the MP2 interaction energies of dimer orientation D.

intermolecular interactions has been highlighted in a number of papers [14, and references therein]. The geometry of a molecule of perfluoromethane was optimized at the MP2/6-311G(d) level. The optimized C–F distance is 1.321 Å, which compares very well with the experimental value of 1.323 Å [10].

3. Results and discussion

3.1. Dimer orientations

A total of nine different orientations of two CF_4 molecules in the dimer relative to each other were chosen (Fig. 1). The interaction energy was calculated for different values of the carbon–carbon separation. The number of configurations considered for the dimer is 130. The internal geometry of the individual CF_4 molecule was frozen in the dimer calculations.

3.2. Effects of basis sets

To evaluate the effect of basis sets, we calculated the intermolecular interaction energies of the dimers C and D at the MP2 level and a number of different basis sets. The interaction energies of the orientations C and D are shown in Figs. 2 and 3, respectively.

It is apparent when looking at Figs. 2 and 3 that there are three different groups of potential energy curves. Each group is characterized by the strength of the interactions. Figs. 2 and 3 tell us that adding diffuse functions to the 6-311G(3d) and the 6-31G(nd) basis sets, $n = 1 - 3$, decreases the corresponding intermolecular interactions. The opposite effect is observed in the case of the 6-311G(d) and 6-311G(2d)
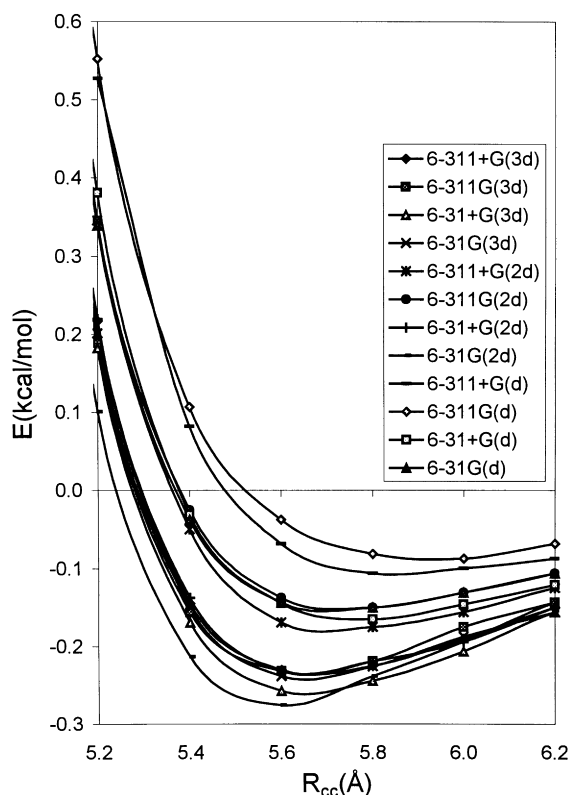
Fig. 3. Basis set effect on the MP2 interaction energies of dimer orientation C.

Fig. 4. Basis set effect on the HF interaction energies of dimer orientation D.

Fig. 5. Basis set effect on the HF interaction energies of dimer orientation C.

basis sets. Regarding the 6-31XG(d) basis sets ($X = +$, 1, 1+), we observe that the presence of additional d functions consistently lowers the corresponding interaction energies. Even though the addition of d functions does lower the interaction energies obtained with the 6-31G(d) basis set, we note that the depth of the potential is largest with the 6-31G(2d) and not with the 6-31G(3d).

In order to understand the details of the basis set effect, the total interaction energy is separated into the repulsive and coulombic energy components evaluated by the Hartree–Fock (HF) method, and the second-order correlation correction energy $E(2)$ to the interaction energy evaluated by the MP2 theory. The results are displayed in Figs. 4–7. It is seen in Figs. 4–7 that the choice of basis set affects both the HF and the $E(2)$ energy terms.

A major component of the interaction energy is the dispersion energy. Dispersion interaction has its
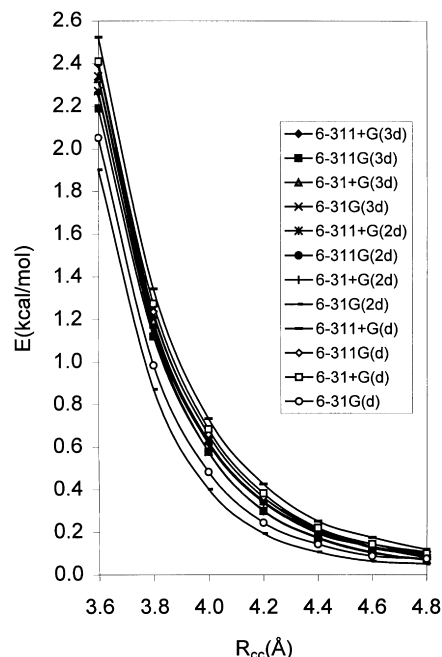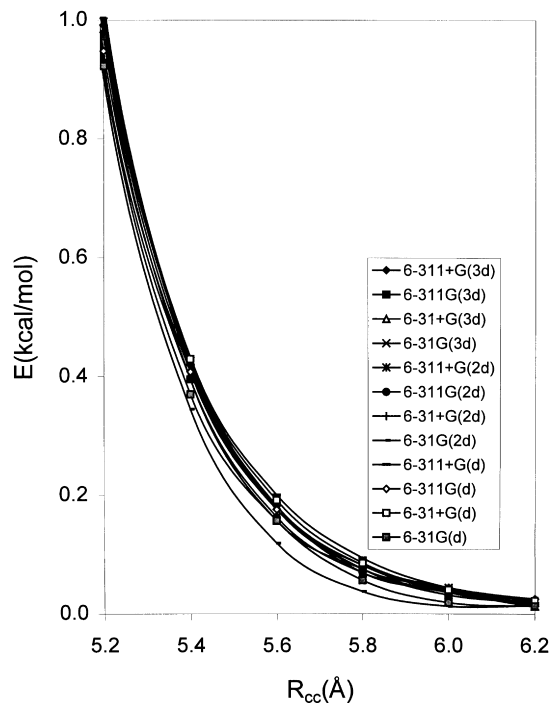
Fig. 6. Basis set effect on the magnitude of the $E(2)$ interaction energies of dimer orientation D.
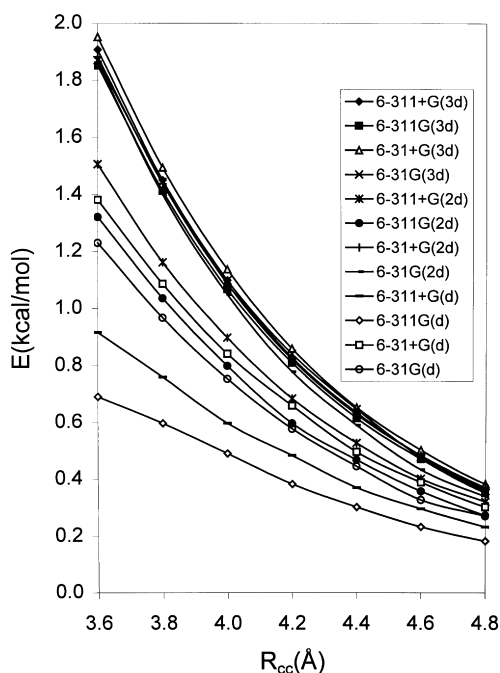

Fig. 7. Basis set effect on the magnitude of the $E(2)$ interaction energies of dimer orientation C.

origins in molecular polarization and electron correlation [10,11]. As the calculated molecular polarizability depends crucially on the used basis set, it is possible to approximately gauge the accuracy of the calculated dispersion energy from the comparison between the calculated and experimental polarizabilities. We calculated the polarizability of CF_4 with several basis sets at both the HF and the MP2 level. The results along with experimental value [12] are shown in Table 1. It should be pointed out that a supermolecule MP2 interaction energy calculation includes the dispersion energy only at the uncoupled HF level. Therefore the most pertinent monomer polarizability is the uncoupled HF polarizability not the MP2 one [15]. Table 1 shows that the calculated polarizabilities get closer to experiment as the number of d functions increases. For 6-31G(nd), $n = 1 - 3$, we also find that, for a given n, the calculated polarizability is improved with the addition of diffuse functions. This effect is less pronounced as more d functions are added. However, it is also seen that the addition of extra valence functions to 6-31G(nd) or
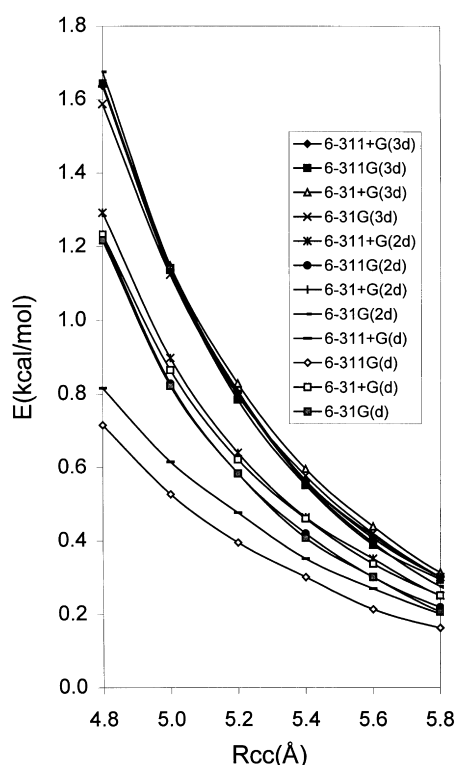
Table 1
CF_4 polarizability calculated at the HF and MP2 levels and some basis sets

Basis set	Polarizability[a]	$(10^{-24}$ cm$^3)$
	HF	MP2
6-31G(d)	1.90	1.97
6-31G(2d)	2.20	2.37 (2.35)
6-31G(3d)	2.42	2.69
6-311G(d)	1.73	1.86
6-311G(2d)	2.00	2.15
6-311G(3d)	2.26	2.45
6-31+G(d)	2.23	2.51
6-31+G(2d)	2.45	2.75
6-31+G(3d)	2.51	2.83
6-311+G(d)	2.09	2.37
6-311+G(2d)	2.29	2.55 (2.52)
6-311+G(3d)	2.46	2.75
Experiment[b]	2.83	

[a] Values in parentheses are calculated at the MP4 level.
[b] Ref. [14].

Table 2

Basis set effect on the HF energy component and on the $E(2)$ energy magnitude. (HF and $E(2)$ energies calculated at a carbon–carbon distance of 4.0 and 5.6 Å for orientation D and C, respectively. 6-31G represents the basis set reference, and the labels d, 2d, 3d, indicate the number of polarization d functions added to 6-31G. The labels 1, +, 1+, indicate, respectively, whether extra valence functions, diffuse functions or both have been added to the basis set that is the header of a given column. Each column shows how the magnitude of the energy component changes with the choice of basis set relative to the header of the column)

6-31G	$E(2)$			HF		
	d	2d	3d	d	2d	3d
Dimer D						
d	0.00			0.00		
2d	0.30	0.00		−0.08	0.00	
3d	0.35	0.05	0.00	0.10	0.18	0.00
1	−0.26	−0.25	−0.03	0.18	0.11	−0.07
+	0.09	0.04	0.04	0.20	0.22	0.05
1+	−0.15	−0.15	0.00	0.25	0.26	0.04
Dimer C						
d	0.00			0.00		
2d	0.09	0.00		−0.04	0.00	
3d	0.12	0.03	0.00	0.02	0.06	0.00
1	−0.09	−0.09	−0.03	0.02	0.04	−0.02
+	0.04	0.02	0.02	0.03	0.06	0.00
1+	−0.03	−0.04	−0.01	0.04	0.06	0.00

$6-31+G(n\mathrm{d})$ consistently lowers the corresponding polarizability.

The $E(2)$ component of dimers C and D are shown in Figs. 6 and 7. The calculated $E(2)$ energies are notoriously affected by the choice of the basis set, more than the HF energy component (Figs. 4 and 5). Figs. 6 and 7 show three groups of curves that can be distinguished in terms of the magnitude of the $E(2)$ energy. This is similar to what we observed in Figs. 2 and 3 for the total MP2 interaction energies. We see that in general the $E(2)$ energy curves correlate well with the calculated polarizabilities.

To illustrate our previous discussion, Table 2 shows in particular the effects of the basis sets on the $E(2)$ and HF energy components of the total interaction energies at the minimum of the potential energy surface of dimers C ($R_{cc} = 5.6$ Å) and D ($R_{cc} = 4.0$ Å). In each column of Table 2, we show how the magnitude of the $E(2)$ and HF energy changes with the choice of basis set relative to the basis set that represents the header of the corresponding column.

It is seen that adding d functions consistently increases the magnitude of $E(2)$. For dimer D, the $E(2)$ energy magnitude calculated by the 6-31G(2d) is larger by 0.30 kcal/mol than that of the 6-31G(d), and that of the 6-31G(3d) is larger by 0.05 kcal/mol than that of the 6-31G(2d). Adding diffuse functions also increases the magnitude of $E(2)$ by 0.09 kcal/mol for the 6-31G(d) basis set, and by 0.04 kcal/mol for the 6-31G(2d) and 6-31G(3d) basis sets, respectively. However, adding either extra valence functions or extra valence functions plus diffuse functions actually decreases the magnitude of the $E(2)$ energy. This effect is large for 6-31G(d) and 6-31G(2d), but it is small or negligible for 6-31G(3d). Similar trends are observed for dimer C.

Regarding the HF energy component, it is observed that for dimer D an additional d function in the 6-31G(d) basis set makes the HF energy less repulsive by 0.08 kcal/mol. However, two more d functions make the HF energy more repulsive by 0.10 kcal/mol. We observe that the addition of extra valence functions and/or diffuse functions makes the HF energy more repulsive, the exception being the 6-311G(3d) basis set where the HF energy is less repulsive by 0.07 kcal/mol than that of the 6-31G(3d) basis set. Again, similar behavior is observed for dimer C.

In short, the basis set dependence of the total interaction energies can be understood as a combination of the basis set dependence of the HF and $E(2)$ energy components, with the $E(2)$ energy playing a major role. The reason why the 6-31G(2d) basis set gives the strongest intermolecular interactions can be traced to the underestimate of the HF energy along with overestimation of the $E(2)$ energy. We observe large changes in the energy components for the 6-31G(d) and 6-31G(2d) basis sets with the addition of diffuse functions, polarization d functions, or both. These changes are relatively small for the 6-31G(3d) basis set.

3.3 Intermolecular potential energy surface

A series of quantum calculations on the nine orientations of CF_4 shown in Fig. 1 were performed to map out points on the intermolecular potential energy surface. The total number of configurations of CF_4 dimer considered is 130. These calculations were carried out using the MP2/6-31+G(3d) method. Although any of the basis sets with 3d polarization

Table 3
Interaction energies (kcal/mol) of CF_4 dimer obtained at the MP2/6-31+G(3d) level of theory

R_{cc} (Å)	Orientation								
	A	B	C	D	E	F	G	H	I
3.40				2.052					
3.60				0.377		2.523			1.581
3.80	1.920			−0.301	0.935	0.546			0.201
4.00	0.377	2.196		−0.508	−0.107	−0.239	2.711		−0.308
4.20	−0.245	0.483		**−0.515**	−0.439	−0.490	0.703		**−0.446**
4.30								2.134	
4.40	−0.439	−0.157		−0.458	**−0.502**	**−0.515**	−0.107	1.192	−0.427
4.60	**−0.458**	−0.345		−0.370	−0.458	−0.458	−0.377	0.157	−0.370
4.80	−0.408	**−0.364**		−0.295	−0.383	−0.383	**−0.420**	−0.226	−0.295
5.00	−0.333	−0.326	1.299	−0.245	−0.301	−0.301	−0.383	**−0.333**	−0.239
5.20	−0.270	−0.264	0.182	−0.188	−0.239	−0.239	−0.314	−0.320	−0.188
5.40	−0.220	−0.213	−0.169	−0.151	−0.195	−0.188	−0.257	−0.276	−0.157
5.60	−0.163	−0.163	**−0.257**	−0.113	−0.144	−0.144	−0.201	−0.226	−0.119
5.80	−0.1255	−0.132	−0.245	−0.094	−0.119	−0.126	−0.157	−0.176	−0.107
6.00	−0.100	−0.113	−0.207	−0.082	−0.094	−0.094	−0.126	−0.144	−0.075
6.20	−0.082	−0.082	−0.157	−0.069	−0.082	−0.075	−0.100	−0.113	−0.063
6.40	−0.075	−0.069	−0.126	−0.050	−0.069	−0.063	−0.075	−0.088	
6.60		−0.057	−0.100				−0.069	−0.069	
6.80			−0.075				−0.050	−0.057	
7.00			−0.063					−0.044	
7.20			−0.050						
7.40			−0.038						

functions could be a reasonable choice to explore the potential energy surface of the CF_4 dimer, we selected the 6-31+G(3d) basis set as its polarizability value is close to experiment. The calculated interaction energies are displayed in Table 3, which shows a minimum for all orientations. The deepest minima are found in orientations D ($R_{cc} = 4.2$ Å) and F ($R_{cc} = 4.4$ Å) each with a depth potential of −0.52 kcal/mol. The weakest intermolecular interaction is found in orientation C with a depth potential of −0.26 kcal/mol, this is 50% that of orientations D and F.

The various points on the ab initio potential energy surface were used to obtain a fit to the Lennard–Jones and Buckingham potential energy functions. Interaction energies larger than 2.00 kcal/mol (a total of five points) were ignored for the fitting. The point charges for Coulomb interactions were obtained from fitting to the electrostatic potential of the monomer CF_4 calculated at the MP2/6-31+G(3d).

Table 4
Parameters derived by fitting the ab initio potential energy surface of CF_4 dimer

Buckingham function[a] $q_c(e)$	B_F	C_F	A_F	B_C	C_C	A_C	rms[a]
0.512	34960	4.0226	176.08	2455	2.395	218.83	0.08
Lennard–Jones function[b]							
$q_c(e)$	ϵ_C	σ_C	ϵ_F	σ_F	rms[c]		
0.512	0.0648	3.9749	0.0255	3.0527	0.10		

[a] B in kcal/mol; C in Å^{-1}; A in kcal Å^6 mol^{-1}.
[b] ϵ in kcal/mol; σ in angstroms.
[c] rms in kcal/mol.

We optimized the interaction parameters of the Lennard–Jones plus charge function,

$$E_{ij} = 4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] + q_i q_j r_{ij}^{-1}$$

and the interaction parameters of the Buckingham plus charge function,

$$E_{ij} = b_{ij}\exp(-c_{ij}/r_{ij}) - a_{ij}/r_{ij}^6 + q_i q_j r_{ij}^{-1}$$

For the Lennard–Jones function, we adopted the traditional combining rules, i.e., $\varepsilon_{CF} = (\varepsilon_{CC}\varepsilon_{FF})^{1/2}$ and $\sigma_{CC} = (\sigma_{CC} + \sigma_{FF})/2$. For the Buckingham function, we used the geometrical mean of the parameters for C/C and F/F interactions to obtain the nonbonding parameters for C/F interaction.

The optimized parameters and the relative mean square errors (rms) are shown in Table 4. The rms errors of 0.08 and 0.10 kcal/mol for Buckingham and Lennard–Jones functions, respectively, are reasonable compared with the well depths in Table 4 that range between 0.26 and 0.52 kcal/mol. The reader should note, however, that parameters derived from fitting the ab initio potential energy surface usually need subsequent adjustment to match experimental data [5,13]. For instance, the parameters can be further tuned to match experimental data of the vapor–liquid coexistence curve of CF_4. This will be the subject of future work. It is also important to highlight that energies of interaction between two closed shell species computed at the MP2 level can turn out to be quite inaccurate. Hence, the effects of increasing the level of correlation is open for further research.

4. Summary

The basis set effects on the nonbonding interaction of the CF_4–CF_4 system have been studied using ab initio molecular orbital calculations with the second-order Møller–Plesset perturbation correction. Different basis sets, corresponding to a systematic improvement of the 6-31G(d) basis set, were considered. It is found that the HF energy component of the interaction energy is somewhat affected by the choice of the basis set. The $E(2)$ energy component of the interaction energy is greatly changed with the choice of the basis set. The potential energy surface of the dimer was explored by calculating the MP2/6-31+G(3d)

interaction energies of 130 different dimer configurations. Nonbonding parameters of the Lennard–Jones and the Buckingham plus charge potential energy functions were obtained by fitting to the ab initio interaction energies.

Acknowledgements

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