

Theoretical Study of CH₄–CH₄, CHF₃–CH₄, CH₄–H₂O, and CHF₃–H₂O Dimers[†]

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Received: May 27, 2009; Revised Manuscript Received: July 7, 2009

We have studied systems with typical hydrogen bonding and others with interaction involving hydrogen. CH₄–CH₄, CH₄–H₂O, CHF₃–CH₄, and CHF₃–H₂O dimers were studied using MPWB1K, PBE1PBE, MP2, and QCISD levels of theory with a large number of basis functions. The Pople 6-31+G(2d), 6-311++G(2d,2p), and 6-311++G(3df,3pd) as well as Dunning augmented aug-cc-pVDZ and aug-cc-pVTZ basis sets were used. The dimer geometries were fully optimized. An optimal basis set was determined for these systems to achieve a suitable compromise between accuracy and computational feasibility. A proper strategy was found for the electronic property calculations of dimers studied: the use of aug-cc-pVDZ as the optimal basis set at MP2 level. Dipole moments, polarizabilities, BSSE effects, and ΔZPE were also analyzed for these dimers.

1. Introduction

The hydrogen bond plays a very important role in the structure, function, and dynamics in chemistry, physics, and biology.^{1–14} The classical view of hydrogen bonding considers the directional interaction between water molecules to be the prototype of all hydrogen bonds. The hydrogen bonding (A–H···B) is generally described as a relatively weak interaction between an electronegative proton acceptor B and a hydrogen atom, which has a covalent binding to the electro-negative proton donor A.

We have studied systems that present particular interaction energies involving hydrogen, ordered as follows: CH₄–CH₄ < CHF₃–CH₄ < CH₄–H₂O < CHF₃–H₂O. The dimers were chosen because of their different Coulombic term contribution on the interaction energy: quadrupole–quadrupole (CH₄–CH₄), quadrupole–dipole (CHF₃–CH₄ and CH₄–H₂O), and dipole–dipole (CHF₃–H₂O). Therefore, our main goal is to find an optimal basis set that gives nearest results to the higher basis set at a lower computational cost to study the whole set of dimers. This study has the aim to provide an optimal basis set and level, introducing a suitable compromise between accuracy and computational feasibility to use in future calculations of potential energy curves, the rovibrational spectra, and spectroscopic constants of these dimers.

This work is organized as follows. In Section 2, we present the computational details used to study CH₄–CH₄, CH₄–H₂O, CHF₃–CH₄, and CHF₃–H₂O dimers. The obtained results and discussion are shown in Section 3. Our conclusions are in Section 4.

2. Computational Details

We have studied CH₄–CH₄, CHF₃–CH₄, CH₄–H₂O, and CHF₃–H₂O dimers using MPWB1K, PBE1PBE, Møller–Plesset

TABLE 1: Notation and Number of Basis Functions (Contracted) Used for the Studied Systems

basis set	notation	CH ₄ CH ₄	CH ₄ H ₂ O	CHF ₃ CH ₄	CHF ₃ H ₂ O
6-31+G(2d)	P1	66	62	135	131
aug-cc-pVDZ	D1	118	100	160	142
6-311++G(2d,2dp)	P2	134	114	185	165
6-311++G(3df,3pd)	P3	222	186	285	249
aug-cc-pVTZ	D2	276	230	345	299

second-order perturbation (MP2), and quadratic configuration interaction with single and double excitations (QCISD) to account for the correlation energy. We have used the 6-31+G(2d), 6-311++G(2d,2p), and 6-311++G(3df,3pd) Pople basis sets as well as the aug-cc-pVDZ and aug-cc-pVTZ Dunning basis set (Table 1). All dimers were completely optimized for each method and basis sets. The QCISD demands high computational resources for the CHF₃–CH₄ and CHF₃–H₂O frequency calculations with largest basis sets; therefore, it was only possible to use the smallest basis set for these dimers. The most stable conformation among the calculated dimer structures was considered for this study. The criteria for optimization and SCF convergence followed the program standard. The frequency was used for the minima characterization. The calculations were performed using the Gaussian03 program package.¹⁵

Force constants were computed at every point, and “very tight” keywords were used for global optimization. We have used the optimizations of CH₄–CH₄, CH₄–H₂O, CHF₃–CH₄, and CHF₃–H₂O dimers to compare and establish a suitable basis set and level to describe these interactions.

The energy difference (ΔE) was calculated as the dimer energy minus the sum of monomer energies for the optimized geometries. The basis set superposition error (BSSE) energy correction was estimated using the counterpoise method.¹⁶ The BSSE correction was calculated on the noncorrected minima structures for the final optimized geometry. The DE was calculated following Hyla–Kryspin,⁵ subtracting the Hartree–Fock from the MP2 interaction energy at the aug-cc-pVTZ basis set (without BSSE correction).

[†] Part of the “Vincenzo Aquilanti Festschrift”.

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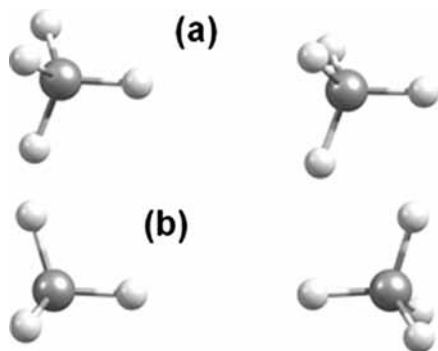


Figure 1. (a) Global and (b) secondary minima for the geometries of CH₄-CH₄ interaction.

We have calculated several properties of these systems, including the isotropic polarizability, α , defined as the mean value of the three diagonal elements of the polarizability tensor

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

and the anisotropy of the dipole polarizability¹⁷ defined as

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 3(\alpha_{xy}^2 + \alpha_{yx}^2 + \alpha_{yz}^2 + \alpha_{zy}^2 + \alpha_{xz}^2 + \alpha_{zx}^2)]^{1/2}$$

For our purpose, the optimal basis set is one that can be used for practical calculations in larger systems and potential energy curves but still gives good results at lowest computational cost relative to the largest basis set data available.

3. Results and Discussion

The results for the optimized dimers are discussed in detail for each case studied in the sections below, and an overview sums up the results and discussion.

3.1. CH₄-CH₄. Figure 1 depicts the global (a) and secondary (b) minima for the geometries of CH₄-CH₄ interaction. The stable global geometry was found for MP2 optimization with ΔE between -0.12 and -0.36 kcal mol⁻¹. ΔE calculated at MP2 level with P2, P3, and D1 basis sets shows less than 28% relative difference from the largest basis set (D2) value (Table 2). In general, it is known that DFT methods have to be used with caution in systems dominated by long-range dispersion forces.^{18–20} We decided to include the MPWB1K (meta hybrid GGA)²¹ and PBE1PBE (hybrid GGA)²² functionals in our calculations because they were among the best for weak intermolecular interactions, as shown in a previous extensive study.¹³ MPWB1K and PBE1PBE ΔE show no significant dependence with the basis sets used probably because of their underestimation of the DE. From Figure 2, BSSE corrections for all methods show the largest values for the P1 and D1 basis sets, whereas P2, D2, and P3 show the smallest BSSE corrections, as expected. MP2 presents values for ΔE (BSSE) and BSSE corrections near the QCISD results. This trend supports the use of MP2 for these systems.

The difference of vibrational zero point energy Δ (ZPE) was calculated as the dimer ZPE minus the sum of monomer energies for the optimized geometries. At the P1 basis set, the Δ (ZPE) for the dimer formation has almost the same value as that for QCISD and MP2. Otherwise, for the P2 basis set, the QCISD Δ (ZPE) value has a significant difference from the MP2 basis set. MP2 is the only method that shows a stable dimer at the

P2, P3, and D2 basis sets considering the sum of ΔE (BSSE) and Δ (ZPE) energies. The D2 basis set ΔE is -0.51 kcal mol⁻¹ without BSSE correction, which is in agreement with the CCSD(T) level extrapolated to the complete basis set limit (-0.51 kcal mol⁻¹).⁷

Considering the C \cdots C, C \cdots H, and H \cdots H distances, QCISD shows the largest dependence on the basis set. The differences between the largest and smallest values of these distances for QCISD are 0.4, 0.4, and 0.1 Å, respectively. Otherwise, MP2, MPWB1K, and PBE1PBE methods show a small dependence on basis sets once these differences are almost 0.2 Å. The results of QCISD using the P2 basis set conflict with the other methods and basis. The experimental C \cdots C distance of the potential minimum spans in the range of 3.84 to 4.27 Å. The potential depth spans in the range of 0.33 to 0.46 kcal mol⁻¹.²³ These results support our calculated data for the CH₄-CH₄ dimer and are in agreement with the theoretical results of Chen et al.²⁴

The total dipole moment average with all basis sets is almost the same, 0.035D (MPWB1K), 0.033D (PBE1PBE), and 0.041D (MP2). The mean square deviation (MSD) of the total dipole moment with all basis sets is 0.008D (MPWB1K), 0.007D (PBE1PBE), and 0.012D (MP2). Therefore, despite the small difference of MSD values regarding all methods, MP2 shows the largest dependence from the basis set. For α , an interesting trend is observed; the Dunning basis sets (D1 and D2) show the largest values, whereas Pople basis sets larger than D1 show the smallest results. The same trend is not observed for the $\Delta\alpha$ value.

Comparing ΔE (BSSE) results with our reference values (MP2/D2), only MP2 results are appropriate for energy calculations with absolute differences (AD) smaller than 30% using D1 and P2 basis sets, whereas with P3 AD is smaller than 10%. The properties, Δ (ZPE), α and $\Delta\alpha$, are well described by the P2 basis set with the smallest deviation from the mean values comparing the three smallest basis sets (P1, D1, and P2). Otherwise, the geometrical distances (C \cdots C, C \cdots H, and H \cdots H) have the smallest variation from the mean values for the P1 basis set.

3.2. CHF₃-CH₄. Figure 3 depicts the global minimum for the CHF₃-CH₄ geometry. Table 3 shows the results for the optimized CHF₃-CH₄ structure. Results at the MP2 level with all basis sets give for CHF₃-CH₄ ΔE (BSSE) values between -0.24 and -0.53 kcal mol⁻¹. Curiously, the ΔE calculated with P1, the smallest basis set, and P2 show basically the same performance in relation to our reference D2 basis set: 53 and 55% of relative difference, respectively. D1 gives better relative performance (34%) than Pople's basis sets, except for the larger P3 (15%) (Table 3). The MP2/P1 ΔE (BSSE) result is only 3% lower than the QCISD/P1 result, justifying the use of the former. ΔE (BSSE) results for MPWB1K range from -0.07 to -0.18 kcal mol⁻¹, whereas those for PBE1PBE show no significant basis set dependence, ranging from -0.13 to -0.18 kcal mol⁻¹. Even for PBE1PBE1/D2, ΔE (BSSE) is 68% lower than our reference value, making MP2/D1 (34% lower) our method of choice for interaction energy of this dimer when faster energy evaluations are desired. Figure 4 shows the largest BSSE correction for the D1 basis set, as also shown for the other dimers.

Considering the C \cdots C and F \cdots H distances, QCISD and MP2 with the P1 basis set show equivalent results, the latter being shorter by just 0.3% (maximum difference of 0.010 Å). DFT results are again conflicting with maximum differences of 0.024 (MPWB1K) and 0.149 Å (PBE1PBE). Relative to our reference MP2 values, MPWB1K/D2 is better than PBE1PBE/D2, show-

TABLE 2: Results for the Global Minimum of CH₄–CH₄ Dimer^a

basis set ^b	method	$\Delta E(\text{BSSE})$ (kcal mol ⁻¹)	$\Delta(\text{ZPE})$ (kcal mol ⁻¹)	$R_{\text{C}\cdots\text{C}}$ (Å)	$R_{\text{C}\cdots\text{H}}$ (Å)	$R_{\text{H}\cdots\text{H}}$ (Å)	dipole (debye)	α (au)	$\Delta\alpha$ (au)
P1	MPWB1K	-0.10	0.52	4.232	3.140	2.960	0.023	27.87	2.94
	PBE1PBE	-0.13	0.28	4.301	3.207	3.024	0.023	28.47	2.75
	MP2	-0.12	0.40	4.196	3.103	2.924	0.023	27.76	2.63
	QCISD	-0.09	0.38	4.223	3.126	2.948	0.025	27.69	2.57
D1	MPWB1K	-0.06	0.68	4.150	3.062	2.880	0.041	33.02	3.50
	PBE1PBE	-0.13	0.48	4.157	3.061	2.887	0.043	34.15	3.54
	MP2	-0.26	0.62	4.008	2.910	2.747	0.053	33.68	3.69
P2	MPWB1K	-0.10	0.56	4.183	3.100	2.880	0.038	30.98	2.84
	PBE1PBE	-0.14	0.25	4.346	3.257	3.071	0.031	31.55	2.62
	MP2	-0.26	0.20	4.126	3.042	2.865	0.036	30.43	2.86
	QCISD	-0.25	0.34	3.796	3.515	3.085	0.001	30.19	3.08
P3	MPWB1K	-0.11	0.57	4.187	3.106	2.906	0.042	32.53	3.40
	PBE1PBE	-0.14	0.46	4.282	3.193	3.010	0.034	33.53	3.07
	MP2	-0.33	0.19	4.045	2.959	2.787	0.046	32.51	3.45
D2	MPWB1K	-0.13	0.70	4.412	3.062	3.080	0.031	33.26	2.83
	PBE1PBE	-0.15	0.26	4.321	3.232	3.046	0.035	33.89	3.23
	MP2	-0.36	0.33	4.018	2.944	2.781	0.048	33.17	3.38
theor		-0.51 ^{7c}							

^a $R_{\text{C}\cdots\text{C}}$ stands for the H₄C \cdots CH₄ interatomic distance; $R_{\text{C}\cdots\text{H}}$ stands for the nearest HC \cdots HC interatomic distance; $R_{\text{H}\cdots\text{H}}$ stands for the nearest H₂CH \cdots HCH₂ interatomic distance. ^b See Table 1 for the notation used. ^c At CCSD(T) level extrapolated to the complete basis set limit with a different geometry.

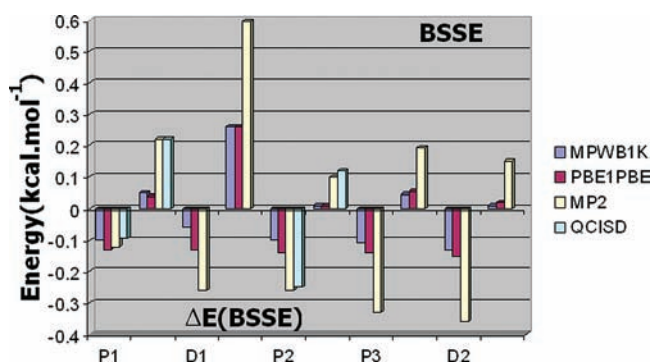


Figure 2. Results for the global minimum of CH₄–CH₄ showing the corrected ΔE and BSSE for all basis sets.



Figure 3. CHF₃–CH₄ dimer obtained at the minimum configuration.

ing differences of 3.5 and 10% respectively; the latter is not chosen by our criteria. However that could just be an artifact of the method because MPWB1K shows such a wild variation for the $\Delta E(\text{BSSE})$ values, making MP2/D1 (0.05% maximum difference) our optimal model of choice for faster or initial geometry optimizations for this system.

Dipole moment and α values show no dependence of basis set for all methods; the MSD values are less than 0.05D and 1.72 au, respectively. Both DFT methods do not show significant variation on the basis set for $\Delta\alpha$. However, MP2 $\Delta\alpha$ shows a dependence on basis set. The MP2/P1 and QCISD/P1 dipoles are very close, whereas DFT methods underestimate dipoles relative to MP2 when the same basis sets are employed. The MP2/P1 polarizability is larger than the QCISD/P1 polarizability by 0.3%. These confirm equivalence between the two models for electrostatic properties, justifying a practical preference for MP2. Here the same trend seen for CH₄–CH₄ is observed, with all People's basis sets underestimating α values. MPWB1K

underestimates whereas PBE1PBE overestimates α values relative to MP2 when the same basis sets are employed, but in general, both methods are within 5% of MP2 results. For the electrostatic properties presented in our study, both DFT methods with the D1 basis give results as good as MP2/D1, all with differences lower than 5% relative to our reference values, and anyone can be used as an optimal model of choice.

3.3. CH₄–H₂O. The CH₄–H₂O optimized structures show two stable minima, one characterized by a HC \cdots HO interaction (Figure 5a), whereas the second with higher energy is characterized by a CH \cdots OH interaction (Figure 5b). The corrected ΔE values for MP2 results are between -0.48 and -0.89 kcal mol⁻¹ (Figure 6). Our results are in agreement with the work of Szczesniak et al.,²⁵ which has calculated MP4 ΔE of -0.708 kcal mol⁻¹. Therefore, for the global minimum, ΔE values for MP2 using P3 and D2 basis sets are in accordance with the experimental and theoretical values found in the literature (Table 4). This minimum energy geometry is in accordance with the study of Raghavendra and Arunan²⁶ at MP2(full)/aug-cc-pVTZ level. Akin-Ojoa and Szalewicz²⁷ using symmetry-adapted perturbation theory (SAPT) have also found two minima.

ΔE calculated at the MP2 level with P2, P3, and D1 basis sets shows less than 24% difference relative to the largest basis set (D2) value (Table 4), whereas P3 and D2 show less than 9% difference relative to the experimental data.²⁸ From Figure 6, the BSSE correction for all methods shows the largest values for the D1 basis sets, whereas P2, D2, and P3 basis sets show the smallest BSSE corrections, as expected. Although this is well established in the literature, it is probably not a general rule because there are some results⁵ for other systems that do not follow this statement. MP2 presents values for $\Delta E(\text{BSSE})$ and BSSE corrections near the QCISD results. This trend supports the use of MP2 for these systems.

At the P1 and P2 basis sets, the $\Delta(\text{ZPE})$ value for the dimer formation has almost the same value for QCISD and MP2. This is different from the trend for the CH₄–CH₄ dimer at the P2 basis set. MP2 is the only method that shows a stable CH₄–H₂O dimer at the P3 and D2 basis sets considering the sum of $\Delta E(\text{BSSE})$ and $\Delta(\text{ZPE})$ energies.

Considering the C \cdots O, C \cdots H, and H \cdots H distances, QCISD, MP2, MPWB1K, and PBE1PBE methods show small variations of these distances of less than 10% (Table 4). The experimental

TABLE 3: Results for the CHF₃–CH₄ Dimer^a

basis set	method	$\Delta E(\text{BSSE})$ (kcal mol ⁻¹)	$\Delta(\text{ZPE})$ (kcal mol ⁻¹)	$R_{\text{C}\cdots\text{C}}$ (Å)	$R_{\text{F}\cdots\text{H}}$ (Å)	dipole (debye)	α (au)	$\Delta\alpha$ (au)
P1	MPWB1K	-0.18	1.69	3.862	3.030	1.660	31.01	3.25
	PBE1PBE	-0.16	0.23	4.135	3.305	1.617	32.74	2.86
	MP2	-0.25	0.45	3.812	2.990	1.751	31.6	1.23
	QCISD	-0.21	0.49	3.813	2.980	1.760	31.5	1.20
D1	MPWB1K	-0.07	1.51	3.861	3.042	1.720	34.82	3.33
	PBE1PBE	-0.16	0.31	3.986	3.130	1.672	35.76	2.55
	MP2	-0.35	0.41	3.741	2.910	1.775	34.80	1.14
P2	MPWB1K	-0.16	1.28	3.845	3.025	1.720	31.39	2.39
	PBE1PBE	-0.13	0.32	4.068	3.101	1.686	33.29	2.51
	MP2	-0.24	0.52	3.739	2.920	1.766	31.70	1.84
P3	MPWB1K	-0.16	1.60	3.847	3.041	1.680	33.46	2.90
	PBE1PBE	-0.17	0.38	4.051	3.226	1.637	35.38	2.79
D2	MPWB1K	-0.14	1.36	3.869	3.044	1.660	34.04	3.30
	PBE1PBE	-0.17	0.24	4.119	3.295	1.620	36.06	2.78
	MP2	-0.53		3.739	2.920	1.700	34.50	2.42

^a $R_{\text{C}\cdots\text{C}}$ stands for the (HC \cdots CH) interaction distance; $R_{\text{H}\cdots\text{F}}$ stands for the CH \cdots FC interatomic distance. C–H1, C–H2, and C–H3 stand for the CH stretching of CH₄. C–H stands for the CH stretching of CHF₃.

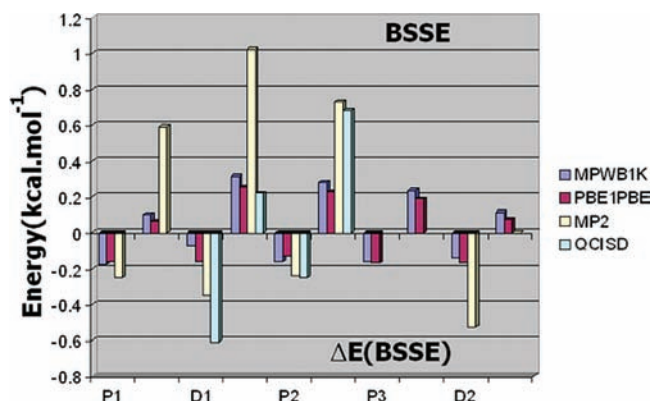


Figure 4. Results for the global minimum of CHF₃–CH₄ showing the corrected ΔE and BSSE for all basis sets.

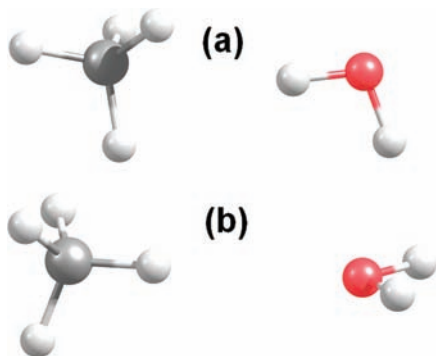


Figure 5. (a) Global and (b) secondary minima for CH₄–H₂O interaction.

microwave spectrum of CH₄–H₂O of Suenram et al.²⁹ supports our global minimum configuration of the CH₄ \cdots HO hydrogen bond (Figure 5a). This is also supported by the experimental works of Dore et al.³⁰ They also obtained the nearest $R_{\text{C}\cdots\text{H}}$ distance of 2.83 Å, whereas our calculated values are between 2.53–2.64 Å. Szczesniak et al.²⁵ have obtained MP4 $R_{\text{C}\cdots\text{O}}$ interatomic distance equal to 3.60 Å using a constrained optimization, which supports our results. For the geometry of Figure 5b the MP2/aug-cc-pVQZ CH₄–H₂O calculation³¹ shows a H \cdots O interaction of 2.601 Å.

The total dipole moment average with all basis sets is almost the same, 2.000D (MPWB1K and PBE1PBE) and 2.083D (MP2). The MSDs of the total dipole moment with all basis sets are 0.049D (MPWB1K), 0.059D (PBE1PBE), and 0.044D

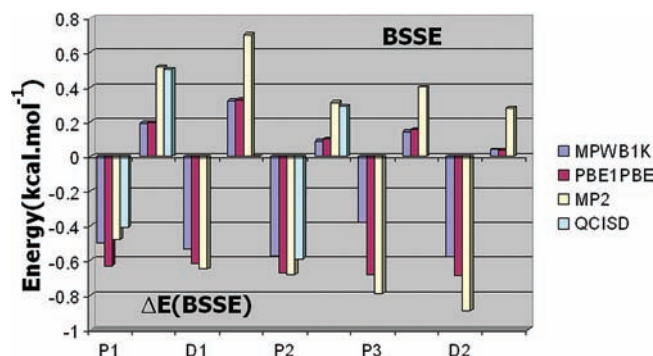


Figure 6. Results for the global minimum of CH₄–H₂O showing the corrected ΔE and BSSE for all basis sets.

(MP2). Therefore, MP2 shows the smallest dependence from the basis set. The maximum difference of dipole moment values is less than 3% in relation to the most extensive basis set at the MP2 level.

The MP2 α values show a large deviation in relation to the largest basis set for the P1 and P2 basis, whereas D1 and P3 show a small deviation. α shows the same trend found for CH₄–CH₄ dimer, where Dunning basis sets (D1 and D2) show the largest values. The same trend is not observed for the $\Delta\alpha$ value. QCISD method has the same trend of MP2 method for all properties described above for the P1 and P2 basis sets.

3.4. CHF₃–H₂O. Table 5 shows the results for the CHF₃–H₂O dimer and Figure 7 depicts the optimized geometry.

For MP2 at the D2 basis set, we have optimized the CHF₃–H₂O and obtained the ΔE of 3.35 kcal mol⁻¹; however, this minimum configuration was not confirmed by frequency analysis because of computational limitations. The results (Table 5) show the smallest ΔE deviation for P2 (1.7%) and D1 (2.8%) in relation to the D2 basis set. The MP2/6-31+G(d,p) value of 3.72 kcal mol⁻¹ with BSSE correction³² is larger than the values for all basis sets used in this work (Table 5). All ΔE results are close to 3.16 kcal mol⁻¹ of Alkorta et al.^{2,33}

From Figure 8, the BSSE correction for all methods shows the largest values for the D1 basis sets, as is also found for the CH₄–CH₄ and CH₄–H₂O dimers. The density functional methods show small dependence with the basis set for BSSE correction mainly for D1, P2, P3, and D2 basis. All methods present $\Delta E(\text{BSSE})$ and BSSE corrections near the QCISD values for the P1 basis set, although MP2 has the nearest results to the QCISD results. This trend supports the use of MP2 for these systems.

TABLE 4: MP2 and QCISD Results for the Global Minimum of CH₄–H₂O Dimer^a

basis set	method	$\Delta E(\text{BSSE})$ (kcal mol ⁻¹)	$\Delta(\text{ZPE})$ (kcal mol ⁻¹)	$R_{\text{C}\cdots\text{O}}$ (Å)	$R_{\text{C}\cdots\text{H}}$ (Å)	$R_{\text{H}\cdots\text{H}}$ (Å)	dipole (debye)	α (au)	$\Delta\alpha$ (au)	
P1	MPWB1K	-0.50	0.82	3.562	2.619	2.448	2.048	21.59	3.59	
	PBE1PBE	-0.63	0.81	3.544	2.590	2.413	2.054	22.23	3.87	
	MP2	-0.48	0.92	3.546	2.592	2.427	2.118	21.60	3.49	
	QCISD	-0.41	0.91	3.581	2.627	2.458	2.087	21.61	3.34	
D1	MPWB1K	-0.53	0.82	3.537	2.609	2.435	1.948	25.55	4.19	
	PBE1PBE	-0.62	0.77	3.530	2.591	2.394	1.932	26.56	4.29	
	MP2	-0.65	0.87	3.484	2.568	2.389	2.018	26.05	4.53	
P2	MPWB1K	-0.57	0.74	3.586	2.641	2.450	2.052	23.48	3.74	
	PBE1PBE	-0.67	0.70	3.554	2.599	2.372	2.061	24.30	4.10	
	MP2	-0.68	0.77	3.511	2.564	2.376	2.125	23.67	3.64	
	QCISD	-0.59	0.74	3.560	2.611	2.414	2.028	23.36	3.67	
P3	MPWB1K	-0.38	0.83	3.576	2.630	2.452	2.006	25.14	3.87	
	PBE1PBE	-0.68	0.82	3.535	2.580	2.385	2.004	25.99	4.20	
	MP2	-0.79	0.69	3.484	2.535	2.372	2.091	25.40	3.97	
D2	MPWB1K	-0.58	0.79	3.581	2.639	2.464	1.955	25.76	3.75	
	PBE1PBE	-0.69	0.71	3.556	2.605	2.413	1.949	26.70	4.12	
	MP2	-0.89	0.79	3.477	2.528	2.355	2.062	26.14	4.02	
exptl/theor		-0.708, ²⁵ -0.8235 ²⁸		3.60, ²⁵ 3.702, ²⁹ 3.509 ²⁸						

^a $R_{\text{C}\cdots\text{O}}$ stands for the (HC \cdots OH) interaction distance; $R_{\text{C}\cdots\text{H}}$ stands for the HC \cdots HO interatomic distance.

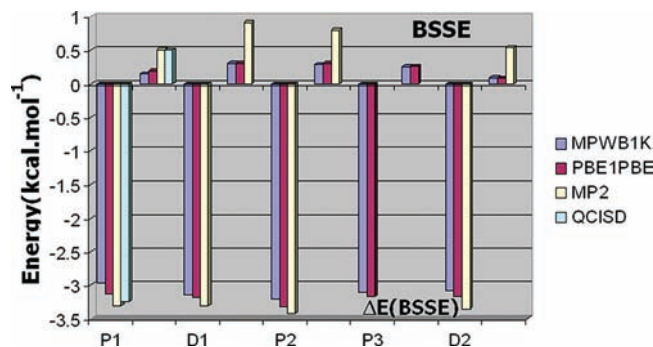
TABLE 5: Results for the CHF₃–H₂O Dimer^a

basis set	method	$\Delta E(\text{BSSE})$ (kcal mol ⁻¹)	$\Delta(\text{ZPE})$ (kcal mol ⁻¹)	$R_{\text{H}\cdots\text{O}}$ (Å)	$R_{\text{C}\cdots\text{H}}$ (Å)	$R_{\text{C}\cdots\text{O}}$ (Å)	$R_{\text{F}\cdots\text{O}}$ (Å)	dipole (debye)	α (au)	$\Delta\alpha$ (au)
P1	MPWB1K	-2.97	0.69	2.269	3.873	3.335	3.908	3.816	24.75	1.78
	PBE1PBE	-3.13	0.77	2.251	3.823	3.326	3.908	3.647	26.10	1.74
	MP2	-3.31	0.60	2.208	3.904	3.281	3.910	4.058	25.28	1.21
	QCISD	-3.24	0.64	2.270	3.989	3.357	3.990	4.139	25.62	1.12
D1	MPWB1K	-3.14	0.73	2.221	3.917	3.306	3.914	4.134	26.25	1.82
	PBE1PBE	-3.18	0.68	2.196	3.914	3.29	3.915	4.084	27.75	1.94
	MP2	-3.31	0.68	2.192	3.949	3.285	3.957	4.167	27.73	1.47
P2	MPWB1K	-3.2	0.66	2.231	3.899	3.305	3.88	4.150	24.20	1.77
	PBE1PBE	-3.32	0.71	2.211	3.885	3.295	3.908	3.992	25.70	1.69
	MP2	-3.42	0.69	2.310	3.098	3.069	2.954	3.242	25.31	2.24
P3	MPWB1K	-3.11	0.77	2.248	3.92	3.324	3.896	4.076	26.05	1.80
	PBE1PBE	-3.17	0.70	2.216	3.94	3.306	3.947	4.021	27.52	1.72
D2	MPWB1K	-3.08	0.79	2.26	3.977	3.341	3.979	4.047	26.71	2.20
	PBE1PBE	-3.17	0.69	2.233	3.969	3.323	3.972	3.988	28.35	1.90
	MP2	-3.35	–	2.211	3.955	3.294	3.952	4.391		
theor				2.16, ³² 2.20–2.29 ³⁴		3.248 ³⁵				

^a $R_{\text{H}\cdots\text{O}}$ stands for the (CH \cdots OH) interaction distance; $R_{\text{C}\cdots\text{H}}$ stands for the HC \cdots HO interatomic distance; $R_{\text{C}\cdots\text{O}}$ stands for the (HC \cdots OH) interaction distance; $R_{\text{F}\cdots\text{O}}$ stands for the (CF \cdots OH) interaction distance.

**Figure 7.** CHF₃–H₂O dimer obtained at the minimum configuration.

Interatomic distances for MP2 show the largest dependence on the basis set in relation to the other methods. The average values for the $R_{\text{H}\cdots\text{O}}$ interatomic distance are 2.246 (MPWB1K), 2.221 (PBE1PBE), and 2.237 Å (MP2). The $R_{\text{C}\cdots\text{H}}$, $R_{\text{C}\cdots\text{O}}$, and $R_{\text{F}\cdots\text{O}}$ interatomic distance average values for the density functional methods are almost 3.900, 3.300, and 3.900 Å, respectively. Otherwise, the MP2 average values for these distances are 3.650, 3.212, and 3.607 Å, respectively. The density functional methods have MSD values less than 0.056 Å for all interatomic distances. MP2 has the smallest MSD value for the $R_{\text{H}\cdots\text{O}}$ of 0.064 Å, whereas the largest MSD value is 0.566 Å for the $R_{\text{F}\cdots\text{O}}$ distance. The results of $R_{\text{H}\cdots\text{O}}$

**Figure 8.** Results for the global minimum of CHF₃–H₂O showing the corrected ΔE and BSSE for all basis sets.

and $R_{\text{C}\cdots\text{O}}$ distances (Table 5) are in accordance with theoretical calculations.^{32,34,35}

MP2 has the largest MSD for the dipole moment, α and $\Delta\alpha$ relative to the methods used, which means that this method is the most dependent on basis set, mainly because of the P2 results.

Table 6 presents the analysis of dispersion energy (DE) estimated from Hartree–Fock and MP2 interaction energies,

TABLE 6: Analysis of Dispersion Energy Estimated from Hartree–Fock and MP2/D2 Interaction Energies without BSSE Correction

dimer	ΔE (kcal mol ⁻¹) MP2	ΔE (kcal mol ⁻¹) HF	dispersion energy (kcal mol ⁻¹)
CH ₄ –CH ₄	-0.50	0.39	-0.89
CHF ₃ –CH ₄	-1.03	0.53	-1.55
CH ₄ –H ₂ O	-1.16	0.22	-1.38
CHF ₃ –H ₂ O	-3.80	-2.62	-1.18

without BSSE corrections, for all dimers. The DE for the CH₄CH₄ dimer of -0.89 kcal mol⁻¹ is the smallest compared with the other dimers. However, the ΔE of CH₄–CH₄ has the largest contribution of DE.

4. Conclusions

We have studied the CH₄–CH₄, CH₄–H₂O, CHF₃–CH₄, and CHF₃–H₂O dimers using MPWB1K, PBE1PBE, MP2, and QCISD methods with Pople and Dunning type basis sets with the purpose of choosing a good compromise between quality and computational cost for geometry, interaction energies, and electrostatic properties. Whereas CH₄–CH₄, CH₄–H₂O, and CHF₃–CH₄ dimers' interaction energies are clearly dominated by the dispersion term, the CHF₃–H₂O dimer is dominated by a Coulombic contribution.

Considering that our reference method for all properties studied was MP2/D2 (aug-cc-pVTZ), our results show that for geometries of all dimers, the combination MP2/P1 (6-31+G(2d)) is a practical choice once it achieves relative differences (RD) smaller than 3%, whereas MP2/D1 (aug-cc-pVDZ) decreases to RD < 0.3% with a considerable increase in computational cost. The former could be used for an initial optimization, followed by the second when better accuracy is needed. Both DFT methods (MPWB1K and PBE1PBE) were not appropriate for the three dimers dominated by dispersion, only achieving an RD close to 3% in the case of CHF₃–H₂O when using PBE1PBE/P1.

Interaction energies dominated by dispersion were well described by MP2/D1 with RD < 34%; both DFT methods were inappropriate. For the CHF₃–H₂O dimer, MP2/P1 showed RD < 2 and RD < 0.05% for MP2/D1. In this case, PBE1PBE with either P1 or D1 reaches RD < 10%. BSSE corrections are smallest for the density functional methods for all studied dimers. The same conclusion was reached by Valdés et al. for interaction on largest molecules with the B3LYP functional including dispersion.³⁶ Although it is well established in the literature that the increase in basis set size decreases the BSSE corrections, our results show that it cannot be used as a general rule. For all dimers, the BSSE corrections for the P1 basis set are smaller than the D1 basis sets values; also, P1 shows smaller values than P2 for dimers involving water.

$\Delta(ZPE)$ for the CHF₃–CH₄ dimer spans in the range of 0.23 to 1.69 kcal mol⁻¹, whereas CH₄–CH₄ is 0.26 to 0.70 kcal mol⁻¹. The MPWB1K method values differ greatly from the other methods being responsible for the highest value in the range.

Dipole moments and polarizabilities were well reproduced with MP2 and both DFT methods to RD < 5% when the D1 basis set was used, except for CHF₃–H₂O PBE1PBE/D1 (RD < 7%).

Acknowledgment. We thank the following Brazilian financial institutions, Finatec, CNPq, and CAPES, for their support. We are also indebted to Prof. Vincenzo Aquilanti from University of Perugia.

References and Notes

- (1) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973.
- (2) Alkorta, I.; Rozas, I.; Elguero, J. *J. Fluorine Chem.* **2000**, *101*, 233.
- (3) Arey, J. S.; Aeberhard, P. C.; Lin, I.-C.; Rothlisberger, U. *J. Phys. Chem. B* **2009**, *113*, 4726.
- (4) Hobza, P.; Havlas, Z. *Theor. Chem. Acc.* **2002**, *108*, 325.
- (5) Hyla-Kryspin, I.; Haufe, G.; Grimme, S. *Chem.–Eur. J.* **2004**, *10*, 3411.
- (6) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
- (7) Li, A. H. T.; Chao, S. D. *THEOCHEM* **2009**, 897, 90.
- (8) Martins, J. B. L.; Politi, J. R. D.; Braga, A. D.; Gargano, R. *Chem. Phys. Lett.* **2006**, *431*, 51.
- (9) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960.
- (10) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784.
- (11) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.
- (12) Wang, X.; Zhou, G.; Tian, A.; Wong, N. B. *THEOCHEM* **2005**, *718*, 1.
- (13) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.
- (14) Zierkiewicz, W.; Jurecka, P.; Hobza, P. *ChemPhysChem* **2005**, *6*, 609.
- (15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.
- (16) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (17) Jeewandara, A. K.; de Silva, K. M. N. *THEOCHEM* **2004**, 686, 131.
- (18) Kohn, W.; Mier, Y.; Makarov, D. E. *Phys. Rev. Lett.* **1998**, *80*, 4153.
- (19) Kristyan, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175.
- (20) Meijer, E. J.; Sprik, M. J. *Chem. Phys.* **1996**, *105*, 8684.
- (21) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908.
- (22) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (23) Matthews, G. P.; Smith, E. B. *Mol. Phys.* **1976**, *32*, 1719.
- (24) Chen, X. R.; Bai, Y. L.; Zhu, J.; Yang, X. D. *Phys. Rev. A* **2004**, *69*.
- (25) Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M.; Cieplak, P. *J. Chem. Phys.* **1993**, *98*, 3078.
- (26) Raghavendra, B.; Arunan, E. *Chem. Phys. Lett.* **2008**, *467*, 37.
- (27) Akin-Ojo, O.; Szalewicz, K. *J. Chem. Phys.* **2005**, 123.
- (28) Cao, Z.; Tester, J. W.; Trout, B. L. *J. Chem. Phys.* **2001**, *115*, 2550.
- (29) Suenram, R. D.; Fraser, G. T.; Lovas, F. J.; Kawashima, Y. *J. Chem. Phys.* **1994**, *101*, 7230.
- (30) Dore, L.; Cohen, R. C.; Schmuttenmaer, C. A.; Busarow, K. L.; Elrod, M. J.; Loeser, J. G.; Saykally, R. J. *J. Chem. Phys.* **1994**, *100*, 863.
- (31) Hyla-Kryspin, I.; Haufe, G.; Grimme, S. *Chem. Phys.* **2008**, *346*, 224.
- (32) Kryachko, E.; Scheiner, S. *J. Phys. Chem. A* **2004**, *108*, 2527.
- (33) Alkorta, I.; Maluendes, S. *J. Phys. Chem.* **1995**, *99*, 6457.
- (34) Zierkiewicz, W.; Michalska, D.; Havlas, Z.; Hobza, P. *ChemPhys-Chem* **2002**, *3*, 511.
- (35) Gu, Y. L.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.
- (36) Valdés, H.; Klusák, V.; Pitoák, M.; Exner, O.; Stary, I.; Hobza, P.; Rulíek, L. *J. Comput. Chem.* **2008**, *29*, 861.