Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supporting Information: Comparison of the performance of dispersion-corrected density functional theory for weak hydrogen bonds

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Contents

1 The $CH_4 \cdot NH_3$ complex

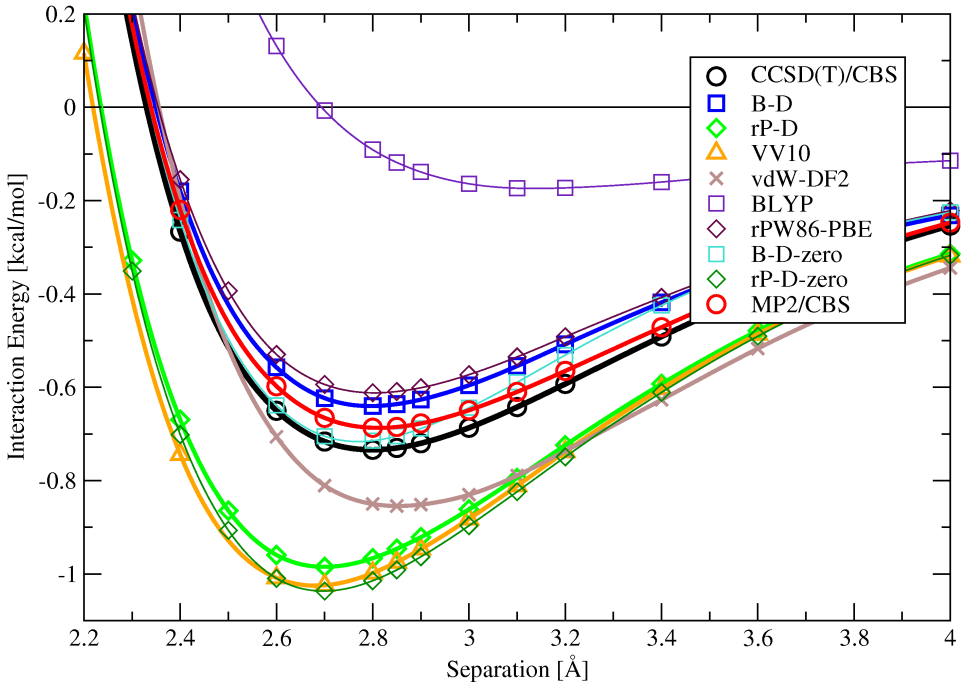

Figure 1 Potential energy curves for $CH_4 \cdot NH_3$.Calculations were performed with the BLYP, rPW86-PBE, B-D-zero, rP-D-zero, B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 1 Binding Energy (ΔE) energy and equilibrium distance for $CH_4 \cdot NH_3$.

Method	R(H–N) [Å]	−ΔE [kcal/mol]
CCSD(T)	2.80	0.73
MP2	2.81	0.69
BLYP	3.13	0.17
rPW86-PBE	2.80	0.61
B-D	2.80	0.64
rP-D	2.70	0.98
B-D-zero	2.77	0.72
rP-D-zero	2.70	1.04
VV10	2.70	1.03
vdW-DF2	2.85	0.85

2 The $Cl_3CH \cdot NH_3$ complex

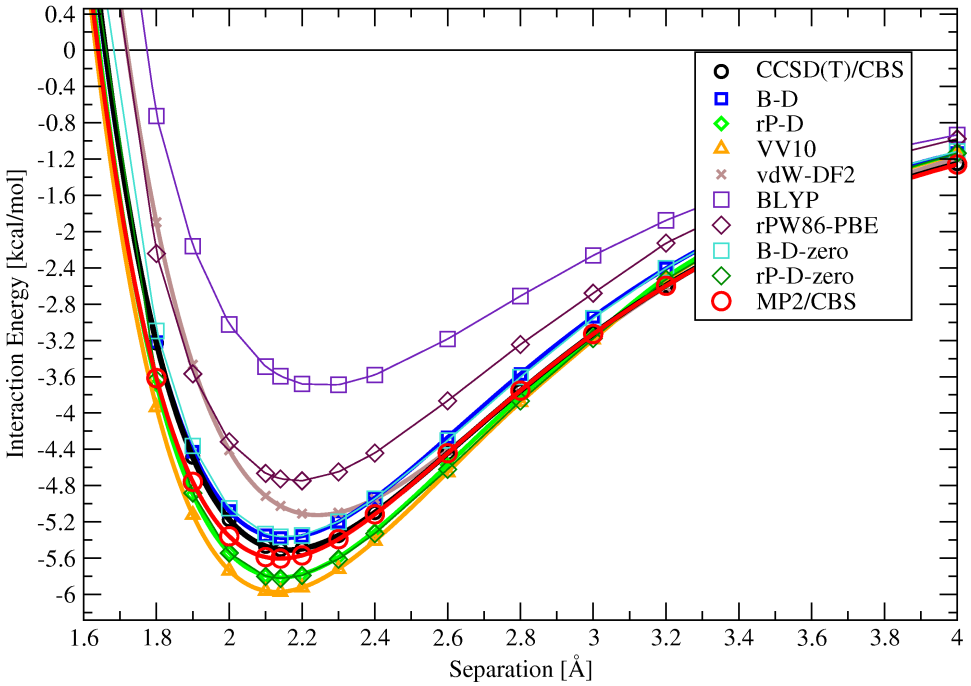

Figure 2 Potential energy curves for $Cl_3CH \cdot NH_3$. Calculations were performed with the BLYP, rPW86-PBE, B-D-zero, rP-D-zero, B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 2 Binding Energy (ΔE) energy and equilibrium distance for $Cl_3CH \cdot NH_3$.

Method	R(H–N) [Å]	−ΔE [kcal/mol]
CCSD(T)	2.16	5.51
MP2	2.14	5.60
BLYP	2.29	3.69
rPW86-PBE	2.20	4.75
B-D	2.15	5.38
rP-D	2.14	5.81
B-D-zero	2.15	5.36
rP-D-zero	2.15	5.82
VV10	2.13	5.97
vdW-DF2	2.24	5.12

3 The $NH_3 \cdot NH_3$ complex

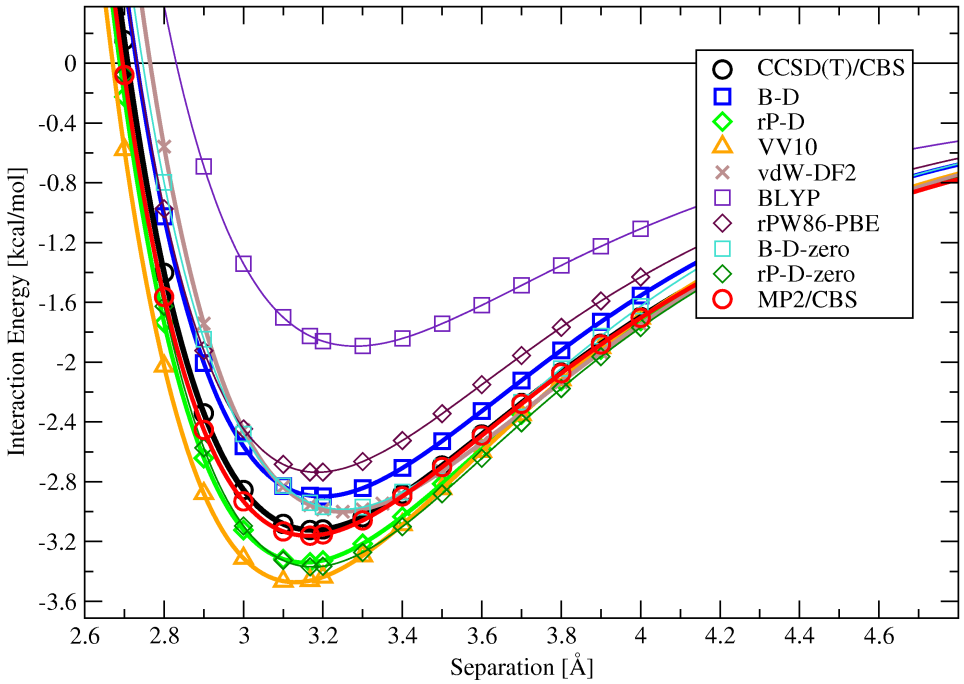

Figure 3 Potential energy curves for $NH_3 \cdot NH_3$. Calculations were performed with the BLYP, rPW86-PBE, B-D-zero, rP-D-zero, B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 3 Binding Energy (ΔE) energy and equilibrium distance for $NH_3 \cdot NH_3$.

Method	R(N–N) [Å]	−ΔE [kcal/mol]
CCSD(T)	3.16	3.12
MP2	3.16	3.16
BLYP	3.28	1.89
rPW86-PBE	3.19	2.74
B-D	3.20	2.90
rP-D	3.15	3.34
B-D-zero	3.25	2.98
rP-D-zero	3.17	3.37
VV10	3.12	3.47
vdW-DF2	3.25	3.00

4 The $CH_3F \cdot C_2H_2$ complex

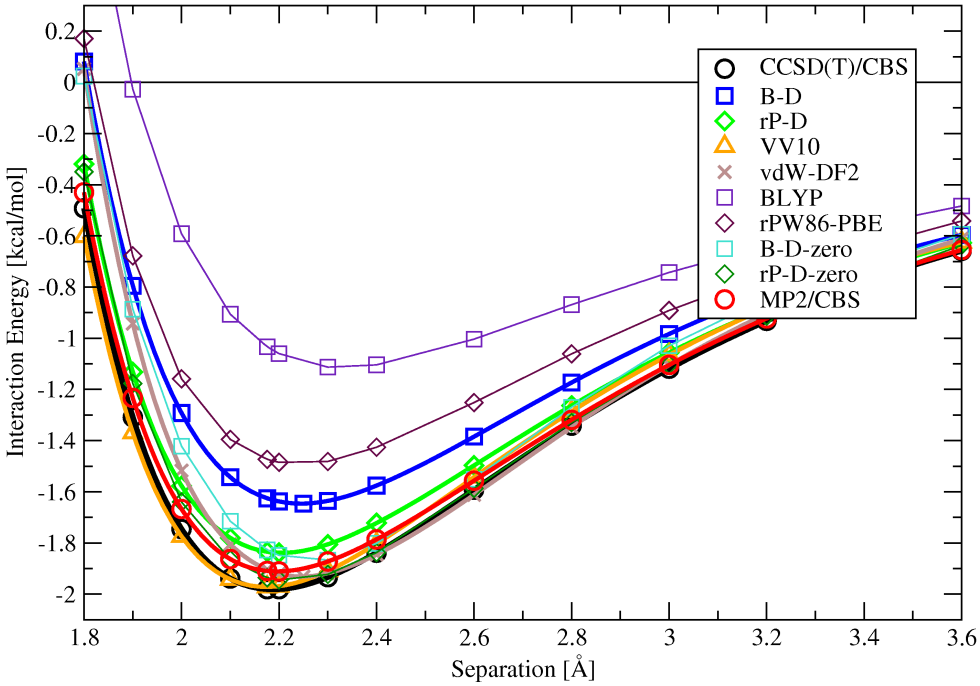

Figure 4 Potential energy curves for $CH_3F \cdot C_2H_2$. Calculations were performed with the BLYP, rPW86-PBE, B-D-zero, rP-D-zero, B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 4 Binding Energy (ΔE) energy and equilibrium distance for $CH_3F \cdot C_2H_2$.

Method	R(H–F) [Å]	−ΔE [kcal/mol]
CCSD(T)	2.20	1.98
MP2	2.20	1.91
BLYP	2.30	1.11
rPW86-PBE	2.20	1.49
B-D	2.25	1.65
rP-D	2.21	1.84
B-D-zero	2.30	1.87
rP-D-zero	2.20	1.94
VV10	2.18	1.97
vdW-DF2	2.25	1.93

5 The $CH_3F \cdot H_2O$ complex

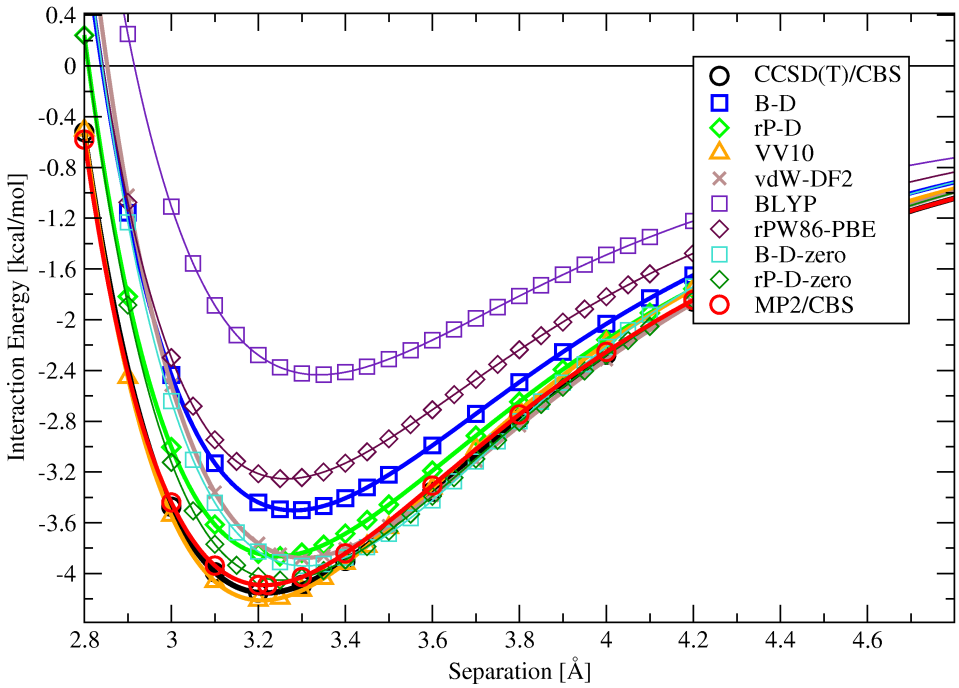

Figure 5 Potential energy curves for $CH_3F \cdot H_2O$. Calculations were performed with the BLYP, rPW86-PBE, B-D-zero, rP-D-zero, B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 5 Binding Energy (ΔE) energy and equilibrium distance for $CH_3F \cdot H_2O$.

Method	R(C–O) [Å]	−ΔE [kcal/mol]
CCSD(T)	3.22	4.15
MP2	3.21	4.09
BLYP	3.34	2.43
rPW86-PBE	3.27	3.25
B-D	3.28	3.50
rP-D	3.24	3.86
B-D-zero	3.31	3.94
rP-D-zero	3.25	4.05
VV10	3.23	4.21
vdW-DF2	3.30	3.88

6 Errors of intermolecular distances and binding energies

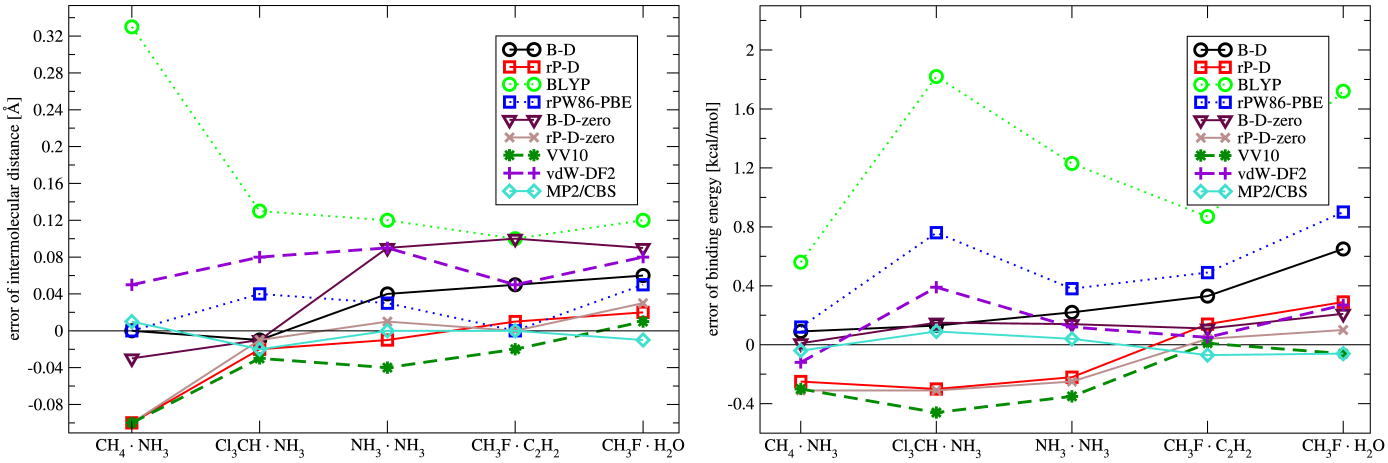

Figure 6 Deviations of DFT-computed intermolecular distances (left) and binding energies (right) from estimated CCSD(T)/CBS(aQ-a5) reference data for all complexes.