

## Supplementary material to: Long-Range Corrected Hybrid Density Functionals with Damped Atom-Atom Dispersion Corrections

Jeng-Da Chai\* and Martin Head-Gordon†

*Department of Chemistry, University of California and  
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

- 
- [1] P. Jurečka, J. Šponer, J. Černý, and P. Hobza, *Phys. Chem. Chem. Phys.* **8**, 1985 (2006).  
[2] J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.* **128**, 084106 (2008).  
[3] Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* **109**, 5656 (2005).  
[4] Y. Zhao, B. J. Lynch, and D. G. Truhlar, *J. Phys. Chem. A* **108**, 2715 (2004).  
[5] Y. Zhao, N. González-García, and D. G. Truhlar, *J. Phys. Chem. A* **109**, 2012 (2005); **110**, 4942(E) (2006).

---

\* Electronic address: [jdchai@berkeley.edu](mailto:jdchai@berkeley.edu)

† Author to whom correspondence should be addressed. Electronic address: [mhg@cchem.berkeley.edu](mailto:mhg@cchem.berkeley.edu)

TABLE I: Interaction energies (in kcal/mol) for the S22 set [1]. The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included. The results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. [2].

Complex [Symmetry]	$\Delta E_{ref}$	$\omega$ B97X-D	B97-D	B3LYP-D	BLYP-D	$\omega$ B97X	$\omega$ B97
<b>Hydrogen bonded complexes</b>							
(NH <sub>3</sub> ) <sub>2</sub> [C <sub>2h</sub> ]	-3.17	-3.07	-3.15	-3.65	-3.44	-3.58	-3.64
(H <sub>2</sub> O) <sub>2</sub> [C <sub>s</sub> ]	-5.02	-4.97	-4.32	-5.30	-4.92	-5.59	-5.64
Formic acid dimer [C <sub>2h</sub> ]	-18.61	-19.30	-17.48	-19.93	-18.50	-19.96	-20.13
Formamide dimer [C <sub>2h</sub> ]	-15.96	-16.16	-14.62	-16.76	-15.63	-16.65	-16.78
Uracil dimer [C <sub>2h</sub> ]	-20.65	-20.44	-18.99	-21.38	-20.22	-20.30	-20.31
2-pyridoxine·2-aminopyridine [C <sub>1</sub> ]	-16.71	-17.06	-16.46	-17.89	-17.28	-16.37	-16.40
Adenine·thymine WC [C <sub>1</sub> ]	-16.37	-16.45	-15.60	-17.27	-16.50	-15.91	-16.05
MSE		-0.14	0.84	-0.81	0.00	-0.27	-0.35
MAE		0.24	0.84	0.81	0.28	0.60	0.63
<b>Dispersion complexes</b>							
(CH <sub>4</sub> ) <sub>2</sub> [D <sub>3d</sub> ]	-0.53	-0.57	-0.54	-0.47	-0.32	-0.57	-0.44
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [D <sub>2d</sub> ]	-1.51	-1.78	-1.48	-1.73	-1.44	-1.77	-1.92
Benzene·CH <sub>4</sub> [C <sub>3</sub> ]	-1.50	-1.68	-1.41	-1.47	-1.23	-1.41	-1.55
Benzene dimer [C <sub>2h</sub> ]	-2.73	-3.19	-2.40	-2.15	-1.91	-1.57	-2.33
Pyrazine dimer [C <sub>s</sub> ]	-4.42	-4.25	-3.88	-3.99	-3.71	-2.86	-3.68
Uracil dimer [C <sub>2</sub> ]	-10.12	-9.79	-9.37	-10.33	-9.68	-7.84	-8.90
Indole·benzene [C <sub>1</sub> ]	-5.22	-5.05	-4.35	-4.18	-3.97	-2.39	-3.58
Adenine·thymine stack [C <sub>1</sub> ]	-12.23	-11.81	-11.42	-12.47	-11.88	-8.40	-10.26
MSE		0.02	0.43	0.18	0.52	1.43	0.70
MAE		0.25	0.43	0.35	0.52	1.51	0.82
<b>Mixed complexes</b>							
Ethene·ethine [C <sub>2v</sub> ]	-1.53	-1.64	-1.63	-1.69	-1.49	-1.67	-1.63
Benzene·H <sub>2</sub> O [C <sub>s</sub> ]	-3.28	-3.50	-3.42	-3.67	-3.30	-3.39	-3.56
Benzene·NH <sub>3</sub> [C <sub>s</sub> ]	-2.35	-2.54	-2.36	-2.48	-2.19	-2.31	-2.46
Benzene·HCN [C <sub>s</sub> ]	-4.46	-4.79	-4.70	-5.18	-4.65	-4.61	-4.89
Benzene dimer [C <sub>2v</sub> ]	-2.74	-2.89	-2.75	-2.80	-2.51	-2.11	-2.38
Indole·benzene T-shape [C <sub>1</sub> ]	-5.73	-5.63	-5.86	-6.07	-5.68	-4.44	-4.82
Phenol dimer [C <sub>1</sub> ]	-7.05	-6.98	-6.03	-7.23	-6.65	-6.49	-6.93
MSE		-0.12	0.06	-0.28	0.10	0.30	0.07
MAE		0.17	0.24	0.28	0.16	0.42	0.33
MSE		-0.08	0.44	-0.28	0.22	0.53	0.16
MAE		0.22	0.50	0.48	0.33	0.87	0.60
rms		0.27	0.69	0.60	0.44	1.30	0.80
Max(-)		-0.69	-0.24	-1.32	-0.57	-1.35	-1.52
Max(+)		0.42	1.66	1.04	1.25	3.83	1.97

TABLE II: Binding energies (in kcal/mol) of several sets of noncovalent interactions. The first three sets are taken from Ref. [3] with monomer deformation energies taken into considerations. The last three sets are taken from Ref. [1] without considering monomer deformation energies. The counter-point corrections are applied for all the cases. The results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. [2].

Complex	$\Delta E_{ref}$	$\omega$ B97X-D	B97-D	B3LYP-D	BLYP-D	$\omega$ B97X	$\omega$ B97
<b>Charge-transfer complexes</b>							
C <sub>2</sub> H <sub>4</sub> ···F <sub>2</sub>	1.06	0.78	3.02	2.20	3.53	1.03	1.09
NH <sub>3</sub> ···F <sub>2</sub>	1.81	1.50	4.33	3.20	5.32	1.93	1.98
C <sub>2</sub> H <sub>2</sub> ···ClF	3.81	3.66	4.57	4.49	5.18	4.43	4.50
HCN···ClF	4.86	4.21	3.87	4.76	5.00	5.32	5.42
NH <sub>3</sub> ···Cl <sub>2</sub>	4.88	4.81	6.36	6.06	7.15	5.18	4.89
H <sub>2</sub> O···ClF	5.36	5.18	5.31	5.98	6.43	6.16	6.21
NH <sub>3</sub> ···ClF	10.62	11.12	14.16	13.54	15.48	11.10	10.49
MSE		-0.16	1.32	1.12	2.24	0.39	0.31
MAE		0.31	1.61	1.15	2.24	0.40	0.35
<b>Dipole-dipole interaction complexes</b>							
H <sub>2</sub> S···H <sub>2</sub> S	1.66	1.54	1.59	1.58	1.50	1.99	1.99
HCl···HCl	2.01	1.69	1.63	1.88	1.77	2.30	2.33
H <sub>2</sub> S···HCl	3.35	3.38	3.46	3.57	3.58	3.90	3.93
CH <sub>3</sub> Cl···HCl	3.55	3.17	3.11	3.52	3.41	3.82	3.97
HCN···CH <sub>3</sub> SH	3.59	3.72	3.65	3.95	3.74	3.99	4.05
CH <sub>3</sub> SH···HCl	4.16	4.87	5.17	5.29	5.36	5.28	5.38
MSE		0.01	0.05	0.25	0.17	0.50	0.56
MAE		0.28	0.35	0.33	0.35	0.50	0.56
<b>Weak interaction complexes</b>							
He···Ne	0.04	0.00	0.09	0.04	0.01	0.01	-0.05
He···Ar	0.06	0.00	0.07	0.01	-0.05	0.05	-0.03
Ne···Ne	0.08	-0.02	0.17	0.14	0.11	-0.02	-0.07
Ne···Ar	0.13	-0.01	0.19	0.16	0.10	0.05	-0.04
CH <sub>4</sub> ···Ne	0.22	0.13	0.30	0.24	0.17	0.10	0.00
C <sub>6</sub> H <sub>6</sub> ···Ne	0.47	0.24	0.50	0.60	0.47	0.30	0.32
CH <sub>4</sub> ···CH <sub>4</sub>	0.51	0.60	0.51	0.51	0.33	0.64	0.55
MSE		-0.08	0.04	0.03	-0.05	-0.05	-0.12
MAE		0.11	0.05	0.04	0.06	0.09	0.13
<b>Hydrogen-bonded DNA base pairs</b>							
G···A HB	-11.30	-13.48	-13.02	-14.19	-13.72	-12.29	-12.44
C···G WC	-30.70	-32.45	-30.00	-33.36	-31.55	-31.92	-32.12
G···C WC	-31.40	-32.28	-29.70	-33.14	-31.28	-31.85	-32.07
MSE		-1.60	0.23	-2.43	-1.05	-0.89	-1.08
MAE		1.60	1.37	2.43	1.13	0.89	1.08
<b>Interstrand base pairs</b>							
G···G IS	-5.20	-5.43	-5.35	-5.30	-5.08	-4.83	-4.70
G···G IS	0.80	1.15	1.04	1.30	1.31	2.21	2.13
C···C IS	3.10	3.29	2.87	3.26	3.06	3.62	3.69
MSE		0.10	-0.05	0.18	0.20	0.77	0.80
MAE		0.25	0.20	0.25	0.23	0.77	0.80
<b>Stacked base pairs</b>							
A···G S	-6.50	-6.66	-6.22	-6.55	-6.25	-3.46	-4.62
C···G S	-12.40	-10.83	-10.11	-10.56	-10.10	-8.57	-9.61
G···C S	-11.60	-11.06	-10.31	-10.71	-10.21	-8.77	-9.69
MSE		0.65	1.29	0.89	1.31	3.23	2.19
MAE		0.76	1.29	0.93	1.31	3.23	2.19
MSE		-0.14	0.49	0.19	0.61	0.51	0.36
MAE		0.43	0.77	0.73	0.90	0.73	0.65
rms		0.68	1.19	1.15	1.51	1.18	0.93

TABLE III: Comparison of errors of different functionals for the reaction energies (in kcal/mol) of the 30 chemical reactions in the NHTBH38/04 and HTBH38/04 database [4, 5]. The results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. [2].

Reactions	$\Delta E_{ref}^a$	$\omega$ B97X-D	B97-D	B3LYP-D	BLYP-D	$\omega$ B97X	$\omega$ B97
H + N <sub>2</sub> O → OH + N <sub>2</sub>	-65.08	4.80	13.72	3.69	12.02	3.72	3.82
H + FCH <sub>3</sub> → HF + CH <sub>3</sub>	-26.64	2.18	-1.14	-0.08	0.63	3.37	4.27
H + F <sub>2</sub> → HF + F	-103.91	-0.70	5.35	0.20	10.08	0.50	2.21
CH <sub>3</sub> + FCl → CH <sub>3</sub> F + Cl	-52.74	-1.02	1.79	-0.03	3.75	-1.85	-2.60
F <sup>-</sup> + CH <sub>3</sub> Cl → FCH <sub>3</sub> + Cl <sup>-</sup>	-32.65	-2.18	-1.16	-2.09	0.36	-1.29	0.78
F <sup>-</sup> ···CH <sub>3</sub> Cl → FCH <sub>3</sub> ···Cl <sup>-</sup>	-26.73	-0.80	1.80	0.41	4.03	-0.23	1.17
OH <sup>-</sup> + CH <sub>3</sub> F → HOCH <sub>3</sub> + F <sup>-</sup>	-20.11	-1.25	0.82	-0.31	0.73	-1.22	-1.80
OH <sup>-</sup> ···CH <sub>3</sub> F → HOCH <sub>3</sub> ···F <sup>-</sup>	-36.24	-2.44	-0.93	-1.54	-0.28	-1.62	-1.36
H + N <sub>2</sub> → HN <sub>2</sub>	3.97	-5.06	-7.59	-7.41	-7.27	-4.30	-3.57
H + CO → HCO	-19.51	-3.28	-5.93	-5.76	-5.87	-2.66	-1.91
H + C <sub>2</sub> H <sub>4</sub> → CH <sub>3</sub> CH <sub>2</sub>	-40.03	-2.47	-1.52	-2.42	0.60	-2.97	-3.52
CH <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	-26.12	-2.90	2.29	0.50	3.48	-4.05	-5.65
HCN → HNC	15.05	-1.85	-0.44	-0.94	0.09	-1.87	-1.97
H + HCl → H <sub>2</sub> + Cl	-3.0	2.71	-2.38	-1.49	-1.28	3.09	3.18
OH + H <sub>2</sub> → H + H <sub>2</sub> O	-16.1	-0.41	2.87	3.23	2.20	-0.84	-1.02
CH <sub>3</sub> + H <sub>2</sub> → H + CH <sub>4</sub>	-3.2	-1.33	3.83	2.29	2.55	-2.30	-2.86
OH + CH <sub>4</sub> → CH <sub>3</sub> + H <sub>2</sub> O	-12.9	0.92	-0.96	0.95	-0.36	1.46	1.84
OH + NH <sub>3</sub> → H <sub>2</sub> O + NH <sub>2</sub>	-9.5	-0.17	-1.89	-0.37	-1.43	0.15	0.23
HCl + CH <sub>3</sub> → Cl + CH <sub>4</sub>	-6.2	1.38	1.45	0.80	1.27	0.79	0.33
OH + C <sub>2</sub> H <sub>6</sub> → H <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub>	-16.5	0.22	-2.33	0.41	-1.31	0.54	1.04
F + H <sub>2</sub> → HF + H	-31.6	-1.09	-0.27	1.81	-0.71	-1.46	-1.96
O + CH <sub>4</sub> → OH + CH <sub>3</sub>	5.6	-0.92	-2.32	-3.14	-5.70	-0.50	0.03
H + PH <sub>3</sub> → PH <sub>2</sub> + H <sub>2</sub>	-20.1	-0.09	-5.25	-3.06	-3.35	0.61	0.74
H + HO → H <sub>2</sub> + O	-2.4	2.26	-1.51	0.85	3.14	2.80	2.82
H + H <sub>2</sub> S → H <sub>2</sub> + HS	-13.8	1.60	-3.73	-2.12	-2.17	2.17	2.32
O + HCl → OH + Cl	-0.6	0.46	-0.87	-2.34	-4.43	0.29	0.36
NH <sub>2</sub> + CH <sub>3</sub> → CH <sub>4</sub> + NH	-14.4	1.53	2.09	3.35	4.55	1.49	1.28
NH <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> → C <sub>2</sub> H <sub>6</sub> + NH	-10.8	2.23	3.46	3.89	5.50	2.41	2.08
C <sub>2</sub> H <sub>6</sub> + NH <sub>2</sub> → NH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub>	-7.0	0.39	-0.44	0.78	0.13	0.39	0.81
NH <sub>2</sub> + CH <sub>4</sub> → CH <sub>3</sub> + NH <sub>3</sub>	-3.3	0.99	0.83	1.22	0.98	1.21	1.50
MSE		-0.21	-0.01	-0.29	0.73	-0.07	0.09
MAE		1.66	2.70	1.92	3.01	1.74	1.97
rms		2.06	3.81	2.56	4.19	2.10	2.36
Max(-)		-5.06	-7.59	-7.41	-7.27	-4.30	-5.65
Max(+)		4.80	13.72	3.89	12.02	3.72	4.27

TABLE IV: Non-hydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set [5]. The results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. [2].

Reactions		$\Delta E_{ref}$	$\omega$ B97X-D	B97-D	B3LYP-D	BLYP-D	$\omega$ B97X	$\omega$ B97
<b>Heavy-atom transfer reactions</b>								
H + N <sub>2</sub> O → OH + N <sub>2</sub>	$V^f$	18.14	17.45	12.93	11.05	8.18	19.22	20.67
	$V^r$	83.22	77.73	64.29	72.44	61.24	80.57	81.93
H + FH → HF + H	$V^f$	42.18	40.54	33.86	30.77	25.76	43.10	44.78
	$V^r$	42.18	40.54	33.86	30.77	25.76	43.10	44.78
H + ClH → HCl + H	$V^f$	18.00	18.24	13.81	12.36	9.74	20.73	23.17
	$V^r$	18.00	18.24	13.81	12.36	9.74	20.73	23.17
H + FCH <sub>3</sub> → HF + CH <sub>3</sub>	$V^f$	30.38	30.10	20.48	21.09	15.32	32.14	33.46
	$V^r$	57.02	54.56	48.26	47.81	41.33	55.41	55.83
H + F <sub>2</sub> → HF + F	$V^f$	2.27	-0.64	-6.26	-7.65	-11.79	0.86	1.96
	$V^r$	106.18	103.97	92.30	96.06	82.04	104.27	103.66
CH <sub>3</sub> + FCl → CH <sub>3</sub> F + Cl	$V^f$	7.43	2.84	-6.56	-2.85	-8.42	3.93	4.62
	$V^r$	60.17	56.60	44.39	49.91	40.57	58.52	59.96
<b>Nucleophilic substitution reactions</b>								
F <sup>-</sup> + CH <sub>3</sub> F → FCH <sub>3</sub> + F <sup>-</sup>	$V^f$	-0.34	-1.36	-5.99	-4.85	-8.95	-2.27	-2.60
	$V^r$	-0.34	-1.36	-5.99	-4.85	-8.95	-2.27	-2.60
F <sup>-</sup> ⋯CH <sub>3</sub> F → FCH <sub>3</sub> ⋯F <sup>-</sup>	$V^f$	13.38	12.91	8.56	10.51	6.82	13.28	13.32
	$V^r$	13.38	12.91	8.56	10.51	6.82	13.28	13.32
Cl <sup>-</sup> + CH <sub>3</sub> Cl → ClCH <sub>3</sub> + Cl <sup>-</sup>	$V^f$	3.10	3.71	-4.14	-2.09	-5.70	4.71	6.21
	$V^r$	3.10	3.71	-4.14	-2.09	-5.70	4.71	6.21
Cl <sup>-</sup> ⋯CH <sub>3</sub> Cl → ClCH <sub>3</sub> ⋯Cl <sup>-</sup>	$V^f$	13.61	14.37	6.99	9.15	5.64	16.09	17.74
	$V^r$	13.61	14.37	6.99	9.15	5.64	16.09	17.74
F <sup>-</sup> + CH <sub>3</sub> Cl → FCH <sub>3</sub> + Cl <sup>-</sup>	$V^f$	-12.54	-13.47	-19.02	-17.72	-20.69	-13.11	-11.72
	$V^r$	20.11	21.36	14.79	17.01	11.60	20.83	20.15
F <sup>-</sup> ⋯CH <sub>3</sub> Cl → FCH <sub>3</sub> ⋯Cl <sup>-</sup>	$V^f$	2.89	3.16	-0.93	0.40	-1.56	4.23	5.39
	$V^r$	29.62	30.70	24.00	26.72	21.14	31.19	30.95
OH <sup>-</sup> + CH <sub>3</sub> F → HOCH <sub>3</sub> + F <sup>-</sup>	$V^f$	-2.78	-3.32	-8.75	-7.40	-11.57	-3.70	-4.05
	$V^r$	17.33	18.05	10.54	13.02	7.80	17.64	17.86
OH <sup>-</sup> ⋯CH <sub>3</sub> F → HOCH <sub>3</sub> ⋯F <sup>-</sup>	$V^f$	10.96	10.50	4.83	7.21	3.18	11.47	11.52
	$V^r$	47.20	49.18	42.01	44.98	39.69	49.33	49.13
<b>Unimolecular and association reactions</b>								
H + N <sub>2</sub> → HN <sub>2</sub>	$V^f$	14.69	12.32	7.59	7.32	5.08	13.99	15.47
	$V^r$	10.72	13.42	11.21	10.76	8.38	14.32	15.06
H + CO → HCO	$V^f$	3.17	3.37	0.87	-0.86	-2.26	4.55	5.65
	$V^r$	22.68	26.16	26.31	24.41	23.12	26.72	27.07
H + C <sub>2</sub> H <sub>4</sub> → CH <sub>3</sub> CH <sub>2</sub>	$V^f$	1.72	2.99	0.58	-1.17	-1.83	4.07	4.94
	$V^r$	41.75	45.49	42.13	41.28	37.60	47.07	48.49
CH <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	$V^f$	6.85	4.57	1.00	3.14	1.45	5.04	4.81
	$V^r$	32.97	33.59	24.84	28.75	24.10	35.21	36.59
HCN → HNC	$V^f$	48.16	46.43	46.68	47.54	46.95	46.29	45.89
	$V^r$	33.11	33.22	32.08	33.43	31.81	33.12	32.80
MSE			-0.42	-6.22	-5.13	-9.32	0.56	1.32
MAE			1.51	6.46	5.24	9.34	1.75	2.31
rms			2.00	7.58	6.17	10.82	2.08	2.82
Max(-)			-5.49	-18.93	-11.41	-24.14	-3.50	-2.81
Max(+)			3.74	3.63	1.73	0.44	5.32	6.74

TABLE V: Hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set [4, 5]. The results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. [2].

Reactions	$\Delta E_{ref}$	$\omega$ B97X-D	B97-D	B3LYP-D	BLYP-D	$\omega$ B97X	$\omega$ B97
H + HCl $\rightarrow$ H <sub>2</sub> + Cl	$V^f$ 5.7	4.22	-1.58	-0.89	-2.60	5.33	6.68
	$V^r$ 8.7	4.51	3.80	3.60	1.69	5.24	6.49
OH + H <sub>2</sub> $\rightarrow$ H + H <sub>2</sub> O	$V^f$ 5.1	2.24	-1.45	0.11	-3.95	2.56	3.27
	$V^r$ 21.2	18.76	11.78	12.98	9.96	19.50	20.39
CH <sub>3</sub> + H <sub>2</sub> $\rightarrow$ H + CH <sub>4</sub>	$V^f$ 12.1	9.14	7.82	7.69	5.96	9.63	10.29
	$V^r$ 15.3	13.67	7.20	8.61	6.60	15.13	16.35
OH + CH <sub>4</sub> $\rightarrow$ CH <sub>3</sub> + H <sub>2</sub> O	$V^f$ 6.7	3.19	-3.11	0.81	-4.02	3.97	4.53
	$V^r$ 19.6	15.17	10.75	12.76	9.24	15.41	15.59
H + H <sub>2</sub> $\rightarrow$ H <sub>2</sub> + H	$V^f$ 9.6	9.22	6.47	4.05	2.67	10.74	12.38
	$V^r$ 9.6	9.22	6.47	4.05	2.67	10.74	12.38
OH + NH <sub>3</sub> $\rightarrow$ H <sub>2</sub> O + NH <sub>2</sub>	$V^f$ 3.2	0.01	-9.03	-3.73	-10.47	1.62	2.83
	$V^r$ 12.7	9.68	2.37	6.14	0.47	10.97	12.10
HCl + CH <sub>3</sub> $\rightarrow$ Cl + CH <sub>4</sub>	$V^f$ 1.7	-1.67	-4.75	-2.95	-5.06	-1.07	-0.47
	$V^r$ 7.9	3.15	0.01	2.45	-0.13	4.34	5.41
OH + C <sub>2</sub> H <sub>6</sub> $\rightarrow$ H <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub>	$V^f$ 3.4	0.33	-6.54	-2.32	-7.57	1.26	1.85
	$V^r$ 19.9	16.61	12.29	13.77	10.24	17.22	17.31
F + H <sub>2</sub> $\rightarrow$ HF + H	$V^f$ 1.8	-3.70	-8.98	-6.25	-11.87	-3.89	-3.76
	$V^r$ 33.4	28.98	22.89	23.54	20.45	29.17	29.80
O + CH <sub>4</sub> $\rightarrow$ OH + CH <sub>3</sub>	$V^f$ 13.7	9.36	3.07	5.97	0.51	9.94	10.45
	$V^r$ 8.1	4.69	-0.21	3.51	0.61	4.85	4.82
H + PH <sub>3</sub> $\rightarrow$ PH <sub>2</sub> + H <sub>2</sub>	$V^f$ 3.1	3.22	-0.82	-1.49	-3.07	4.62	5.88
	$V^r$ 23.2	23.41	24.52	21.67	20.38	24.11	25.25
H + HO $\rightarrow$ H <sub>2</sub> + O	$V^f$ 10.7	8.78	1.76	4.04	1.48	9.79	10.68
	$V^r$ 13.1	8.92	5.67	5.58	0.74	9.38	10.26
H + H <sub>2</sub> S $\rightarrow$ H <sub>2</sub> + HS	$V^f$ 3.5	4.07	0.12	-0.88	-2.54	5.54	6.94
	$V^r$ 17.3	16.27	17.65	15.03	13.42	17.16	18.42
O + HCl $\rightarrow$ OH + Cl	$V^f$ 9.8	5.63	-5.26	0.92	-8.82	7.07	14.21
	$V^r$ 10.4	5.77	-3.79	3.86	-3.79	7.38	14.45
NH <sub>2</sub> + CH <sub>3</sub> $\rightarrow$ CH <sub>4</sub> + NH	$V^f$ 8.0	5.67	0.83	4.59	1.81	6.50	6.95
	$V^r$ 22.4	18.54	13.14	15.64	11.66	19.42	20.07
NH <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> $\rightarrow$ C <sub>2</sub> H <sub>6</sub> + NH	$V^f$ 7.5	7.38	2.91	6.10	3.54	8.48	8.82
	$V^r$ 18.3	15.95	10.26	13.01	8.84	16.87	17.54
C <sub>2</sub> H <sub>6</sub> + NH <sub>2</sub> $\rightarrow$ NH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub>	$V^f$ 10.4	8.81	3.43	6.80	3.04	10.16	11.01
	$V^r$ 17.4	15.42	10.88	13.02	9.91	16.77	17.21
NH <sub>2</sub> + CH <sub>4</sub> $\rightarrow$ CH <sub>3</sub> + NH <sub>3</sub>	$V^f$ 14.5	11.39	6.45	9.56	6.03	12.64	13.49
	$V^r$ 17.8	13.70	8.93	11.64	8.35	14.72	15.29
<i>s-trans cis</i> -C <sub>5</sub> H <sub>8</sub> $\rightarrow$ <i>s-trans cis</i> -C <sub>5</sub> H <sub>8</sub>	$V^f$ 38.4	39.06	34.63	37.81	34.72	41.44	42.84
	$V^r$ 38.4	39.06	34.63	37.81	34.72	41.44	42.84
MSE		-2.52	-7.33	-5.39	-8.89	-1.51	-0.34
MAE		2.64	7.41	5.39	8.89	2.24	2.24
rms		3.04	8.09	5.80	9.52	2.58	2.62
Max(-)		-5.50	-15.06	-9.86	-18.62	-5.69	-5.56
Max(+)		0.66	1.32	-0.59	-2.82	3.04	4.44

TABLE VI: Comparison of errors of different functionals for the intermolecular bond lengths (in Å) of the 12 weakly bound complexes on the S22 set [1]. For the hydrogen bonded complexes, the hydrogen bond lengths are computed, while for other complexes, the distances of the centers of mass of the monomers are computed.

Complex [Symmetry]	Reference	MP2	$\omega$ B97X-D	B97-D	B3LYP-D	BLYP-D	$\omega$ B97X	$\omega$ B97
<b>Hydrogen bonded complexes</b>								
(NH <sub>3</sub> ) <sub>2</sub> [C <sub>2h</sub> ]	2.504	0.010	0.032	0.043	-0.006	0.002	-0.019	-0.033
(H <sub>2</sub> O) <sub>2</sub> [C <sub>s</sub> ]	1.952	-0.017	-0.017	0.014	-0.039	-0.028	-0.030	-0.029
Formic acid dimer [C <sub>2h</sub> ]	1.670	-0.015	-0.003	-0.019	-0.019	-0.020	0.008	0.019
Formamide dimer [C <sub>2h</sub> ]	1.841	-0.011	0.005	0.003	-0.015	-0.014	0.015	0.020
MSE		-0.008	0.005	0.010	-0.020	-0.015	-0.006	-0.006
MAE		0.013	0.014	0.020	0.020	0.016	0.018	0.025
<b>Dispersion complexes</b>								
(CH <sub>4</sub> ) <sub>2</sub> [D <sub>3d</sub> ]	3.718	-0.113	-0.198	0.042	-0.267	-0.200	-0.231	-0.362
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [D <sub>2d</sub> ]	3.718	-0.066	-0.064	-0.114	-0.218	-0.194	-0.080	-0.140
Benzene·CH <sub>4</sub> [C <sub>3</sub> ]	3.716	-0.175	-0.088	-0.041	-0.133	-0.103	0.043	-0.090
Benzene dimer [C <sub>2h</sub> ]	3.765	-0.231	0.056	0.125	0.043	0.079	0.177	0.077
MSE		-0.146	-0.074	0.003	-0.144	-0.104	-0.022	-0.129
MAE		0.146	0.101	0.080	0.166	0.144	0.133	0.167
<b>Mixed complexes</b>								
Ethene·ethine [C <sub>2v</sub> ]	4.422	-0.102	-0.050	-0.092	-0.140	-0.124	-0.073	-0.102
Benzene·H <sub>2</sub> O [C <sub>s</sub> ]	3.380	-0.144	-0.144	-0.084	-0.162	-0.117	-0.129	-0.192
Benzene·NH <sub>3</sub> [C <sub>s</sub> ]	3.560	-0.204	-0.082	-0.093	-0.171	-0.140	-0.059	-0.131
Benzene·HCN [C <sub>s</sub> ]	3.950	0.024	0.024	-0.032	-0.074	-0.056	0.003	-0.143
MSE		-0.107	-0.063	-0.075	-0.137	-0.109	-0.065	-0.142
MAE		0.119	0.075	0.075	0.137	0.109	0.066	0.142
MSE		-0.087	-0.044	-0.021	-0.100	-0.076	-0.031	-0.092
MAE		0.093	0.064	0.058	0.107	0.090	0.072	0.111
rms		0.121	0.085	0.071	0.136	0.111	0.100	0.145
Max(-)		-0.231	-0.198	-0.114	-0.267	-0.200	-0.231	-0.362
Max(+)		0.024	0.056	0.125	0.043	0.079	0.177	0.077