Supplementary Tables of TAEs, EAs, IPs, PAs, and BDEs for "Unrestricted coupled cluster and Brueckner doubles variations of W1 theory"

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I. Test Sets Used

The atoms, ions, and molecules of the G2-1[1 2 3] and G2-2[4 5] test sets employed in the original assessment of W1 theory [6 7 8] are retained in this study to facilitate comparisons. This subset consists of 81 heats of formation, 57 electron affinities (EAs), 76 ionization potentials (IPs), and 8 proton affinities (PAs).[6 7 8] Experimental references are taken from the standard compilations of thermochemical tables.[9 10 11 12 13 14 15 16 17 18] All calculations employed the Gaussian 09 program.[19] Spin-orbit corrections were taken from Ref. 7.

Additional error analyses are presented at the bottom of Tables S-III, S-V, S-VI, S-VII, and S-VIII, wherein species with experimental uncertainties larger than 0.24 kcal/mol are excluded from the statistics. This allows for a more precise evaluation of the performance of the W1 variants. The criterion for this threshold is based on the target "benchmark accuracy" of 1 kJ/mol (0.24 kcal/mol) of W1 theory. [6 7 8] A careful discussion on the sizeable deviations of theory from experiment for some problematic cases can be found in Ref. 7. Optimized UB3LYP/cc-pVTZ+1*d* geometries and W1U, W1Usc, and W1BD energy components for all species are available in the accompanying "geometries.txt" and "components.pdf" files as Supporting Information, respectively.

II. Total Atomization Energies

The total atomization energies (TAEs) are obtained from the difference between gas-phase enthalpies of formation of a molecule and its constituent atoms. The experimental heats of formation at 298K of the atoms and molecules are given in Tables S-I and S-II, respectively. For closed-shell species, the small difference in TAEs of W1U, W1Usc, and W1(RO) result from the trivial differences in the calculated enthalpies of the constituent atoms (Table S-I).

The uncertainty in the experimental and calculated TAEs includes contributions from both the uncertainties in the experimental atomic heats of formation, σ_A, (Table S-I) and the uncertainty in the experimental molecular heat of formation, σ_j (Table S-II):

$$\sigma_{\text{expt}} = \left[\sigma_{\text{j}}^{2}(\text{molecule}) + \sum_{\text{A}}^{\text{A in j}} \sigma_{\text{A}}^{2}(\text{atoms in j}) \right]^{\frac{1}{2}} \qquad \text{(S.1)}$$

The deviations of calculated TAEs from experimental values in the G2-1 and G2-2 test sets are given in Tables S-III and S-IV, respectively. A separate error analysis excluding the strongly multireference systems, C_2 and O_3, is presented at the bottom of Table S-VI (see discussion in main article).

Table S-I. Error in calculated $\langle S^2 \rangle$, W1U, W1Usc, W1BD, and W1(RO) enthalpies (hartree au), and experimental heats of formation (kcal/mol) for atoms.

Atom	UHF $\Delta\langle S^2 \rangle$ [a]	UBDRef $\Delta\langle S^2 \rangle$ [a]	W1U H_{298}	W1Usc H_{298}	W1BD H_{298}	W1(RO) H_{298}	Experimental $\Delta_f H_{298}$ [b]
H	0.0000	0.0000	-0.497634	-0.497634	-0.497634	-0.497634	52.103± 0.001
Li	0.0000	0.0000	-7.469691	-7.469691	-7.469691	-7.469692	38.07± 0.24
Be	0.0000	0.0000	-14.661045	-14.661045	-14.661067	-14.661045	77± 1 [c]
B	0.0113	0.0056	-24.651372	-24.651443	-24.651371	-24.651399	137.4± 0.2 [d]
C	0.0104	0.0058	-37.850506	-37.850571	-37.850513	-37.850539	171.29± 0.11
N	0.0079	0.0044	-54.608816	-54.608866	-54.608828	-54.608841	112.913± 0.012 [e]
O	0.0094	0.0059	-75.108901	-75.108960	-75.108878	-75.108948	59.56± 0.02
F	0.0042	0.0028	-99.809130	-99.809156	-99.809057	-99.809167	18.98± 0.07
Na	0.0001	0.0001	-162.323325	-162.323325	-162.323244	-162.323325	25.7± 0.2
Al	0.0206	0.0086	-242.641272	-242.641402	-242.641220	-242.641303	78.9± 1.0
Si	0.0157	0.0079	-289.830543	-289.830642	-289.830522	-289.830622	108.19± 0.38 [f]
P	0.0007	0.0004	-341.946595	-341.946599	-341.946603	-341.946687	75.6± 0.2
S	0.0136	0.0059	-399.062773	-399.062858	-399.062789	-399.062860	66.25± 0.04 [c]
Cl	0.0108	0.0052	-461.431301	-461.431369	-461.431321	-461.431357	28.991± 0.002

[a] $\langle S^2 \rangle$ values calculated with the aug-cc-pVQZ+2*d*1*f* basis set, where "+2*d*1*f*" denotes additional high-exponent *d* and *f* functions for accommodating inner-shell correlation effects.
[b] From Reference 9 unless otherwise noted.
[c] Reference 10.
[d] E. Storms and B. Mueller, J. Phys. Chem. **81**, 318 (1977).
[e] X. Tang, Y. Hou, C. Y. Ng, and B. Ruscic, J. Chem. Phys. **123**, 74330 (2005).
[f] J. M. L. Martin and P. Taylor, J. Phys. Chem. **103**, 4427 (1999).

Table S-II. Experimental heats of formation (298 K, kcal/mol) used to calculate total atomization energies of species in G2-1 and G2-2 test sets.[a]

Species	$\Delta_f H_{298}$	Species	$\Delta_f H_{298}$
G2-1		P_2	34.42± 0.48[f]
LiH	33.61± 0.01	S_2	30.74± 0.07[f]
BeH	81.70± 1.00[b]	Cl_2	0.00± 0.00[j]
CH	142.50± 0.19[c]	NaCl	-43.36± 0.50
CH_2 ($^3B_1$)	93.30± 0.30[d]	SiO	-24.00± 2.01
CH_2 ($^1A_1$)	102.30± 0.30[d]	CS	66.90± 0.10[c]
CH_3	34.99± 0.07[c]	SO	1.20± 0.31
CH_4	-17.83± 0.07[e]	ClO	24.19± 0.50
NH	85.21± 0.41[c]	FCl	-13.20± 0.10
NH_2	45.10± 0.07[c]	Si_2H_6	19.05± 0.31[c]
NH_3	-10.98± 0.08[f]	CH_3Cl	-19.60± 0.12[c]
OH	8.91± 0.07[g]	CH_3SH	-5.46± 0.14[k]
OH_2	-57.80± 0.01[f]	HOCl	-17.81± 0.50
FH	-65.32± 0.17[f]	SO_2	-70.89± 0.05[c]
SiH_2 ($^1A_1$)	65.33± 1.20[e]		
SiH_2 ($^3B_1$)	86.20± 1.00[h]	***G2-2***	
SiH_3	47.90± 0.81[c]	BF_3	-271.50± 0.20[q]
SiH_4	8.20± 0.36[c]	BCl_3	-96.30± 0.50
PH_2	33.10± 0.60[c]	CF_4	-223.00± 0.20[e]
PH_3	1.29± 0.41	OCS	-33.90± 0.50[e]
H_2S	-4.92± 0.12[f]	CS_2	28.01± 0.24[c]
HCl	-22.06± 0.02[f]	N_2O	19.60± 0.10[c]
Li_2	51.60± 0.72	ClNO	12.60± 0.10[e]
LiF	-81.45± 2.01	NF_3	-31.60± 0.31
C_2H_2 (acetylene)	54.54± 0.17[i]	F_2O	5.90± 0.41[e]
C_2H_4 (ethylene)	12.50± 0.07[c]	CH_2F_2	-108.10± 0.20[e]
C_2H_6 (ethane)	-20.08± 0.10[e]	CH_3CN	17.70± 0.10[q]
CN	105.23± 1.20[e]	HCOOH	-90.50± 0.10[e]
HCN	31.55± 0.96[e]	C_2H_4O (oxirane)	-12.57± 0.14[c]
CO	-26.42± 0.04[e]	HCOCOH (glyoxal)	-50.70± 0.20[m]
HCO	9.99± 0.19[c]	CH_3OCH_3	-44.00± 0.10[m]
H_2CO	-25.98± 0.12[e]	C_2H_5Cl	-26.80± 0.20[m]
CH_3OH	-48.21± 0.05[c]	CH_3COCH_3	-51.91± 0.10[c]
N_2	0.00± 0.00[j]	HS	34.20± 0.70[n]
H_2NNH_2	22.75± 0.12[e]	CCH	135.90± 0.19[i,o]
NO	21.61± 0.05[c]	C_2H_3	71.61± 0.79[c]
O_2	0.00± 0.00[j]	CH_3CO	-2.39± 0.29[p]
HOOH	-32.48± 0.05[e]	CH_2OH (^2A)	-4.11± 0.31[c]
F_2	0.00± 0.00[j]	CH_3CH_2O	-3.70± 0.80[q]
CO_2	-94.05± 0.03[f]	CH_3S	29.80± 0.40[q]
Na_2	34.01± 0.05[c]	C_2H_5	28.40± 0.50[r]
Si_2	140.99± 3.11	NO_2	8.20± 0.10[e]

[a]From Reference 11 unless otherwise indicated.

[b]Reference 12.
[c]Reference 9.
[d]M. Litorja. and B. Ruscic, J. Chem. Phys. **108**, 6748 (1998).
[e]Reference 13.
[f]Reference 10.
[g]B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, X. Qian, C. Ng, J. Liu, W. Chen, and D. W. Schwenke, J. Phys. Chem. A **106**, 2727 (2002).
[h]J. Berkowitz, J. P. Greene, H. Cho, and B. Ruscic, J. Chem. Phys. **86**, 1235 (1987).
[i]Reference 14.
[j]Standard state.
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[l]X. An, M. Mansson, J. Chem. Thermodyn. **15**, 287 (1983).
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[n]J. Berkowitz, G. B. Ellison, and D. Gutman, J. Phys. Chem. **98**, 2744 (1994).
[o]D. H. Mordaunt and M. N. R. Ashfold, J. Chem. Phys. **101**, 2630 (1994)
[p]J. T. Niiranen, D. Gutman, and L. N. Krasnoperov, J. Phys. Chem. **96**, 5881 (1992); C. W. Bauschlicher, Jr., J. Phys. Chem. **98**, 2564 (1994).
[q]J. Berkowitz, G. B. Ellison, and D. Gutman, J. Phys. Chem. **98**, 2744 (1994) and references therein.
[r]W. Tsang, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman (Blackie Academic and Professional, London, 1996).

Table S-III. Error in $\langle S^2 \rangle$, and deviation of total atomization energies (298 K, kcal/mol) from experiment for select molecules from the G2-1 test set.[a]

	W1U $\Delta\langle S^2\rangle$		W1BD $\Delta\langle S^2\rangle$		Deviation (Expt. – Theory)				
Molecule	Reactant	Product	Reactant	Product	W1U	W1Usc	W1BD	W1RO	Experiment[b]
LiH	0.0000	0.0000	0.0000	0.0000	-0.41	-0.41	-0.41	-0.41	56.57 ± 0.24
BeH	0.0020	0.0000	0.0015	0.0000	-0.93	-0.94	-0.92	-0.93	47.84 ± 1.23 [c]
CH	0.0098	0.0104	0.0048	0.0058	-0.09	-0.08	-0.08	-0.09	80.90 ± 0.23 [d]
CH_2 ($^3B_1$)	0.0168	0.0104	0.0081	0.0058	0.09	0.07	0.08	0.10	182.20 ± 0.32 [e]
CH_2 ($^1A_1$)	0.0000	0.0104	0.0000	0.0058	0.25	0.29	0.27	0.27	173.20 ± 0.32 [e]
CH_3	0.0118	0.0104	0.0054	0.0058	-0.33	-0.34	-0.34	-0.33	292.61 ± 0.14 [d]
CH_4	0.0000	0.0104	0.0000	0.0058	-0.36	-0.32	-0.36	-0.34	397.54 ± 0.14 [f]
NH	0.0168	0.0079	0.0086	0.0044	0.48	0.45	0.49	0.47	79.81 ± 0.41 [d]
NH_2	0.0098	0.0079	0.0049	0.0044	-0.88	-0.89	-0.87	-0.89	172.02 ± 0.07 [d]
NH_3	0.0000	0.0079	0.0000	0.0044	-0.35	-0.32	-0.33	-0.34	280.20 ± 0.08 [g]
OH	0.0072	0.0094	0.0041	0.0059	-0.18	-0.17	-0.15	-0.18	102.75 ± 0.07 [h]
OH_2	0.0000	0.0094	0.0000	0.0059	-0.43	-0.40	-0.38	-0.40	221.56 ± 0.03 [g]
FH	0.0000	0.0042	0.0000	0.0028	-0.31	-0.29	-0.26	-0.28	136.40 ± 0.18 [g]
SiH_2 ($^1A_1$)	0.0000	0.0157	0.0000	0.0079	-1.06	-1.00	-1.06	-1.01	147.07 ± 1.26 [f]
SiH_2 ($^3B_1$)	0.0066	0.0157	0.0037	0.0079	-0.38	-0.35	-0.40	-0.37	126.20 ± 1.07 [i]
SiH_3	0.0052	0.0157	0.0032	0.0079	-0.82	-0.77	-0.84	-0.78	216.61 ± 0.90 [d]
SiH_4	0.0000	0.0157	0.0000	0.0079	-1.05	-0.99	-1.06	-1.00	308.41 ± 0.52 [d]
PH_2	0.0207	0.0007	0.0076	0.0004	-1.16	-1.24	-1.17	-1.15	146.75 ± 0.64 [d]
PH_3	0.0000	0.0007	0.0000	0.0004	0.20	0.20	0.20	0.25	230.66 ± 0.47
H_2S	0.0000	0.0136	0.0000	0.0059	-0.35	-0.30	-0.36	-0.30	175.38 ± 0.13 [g]
HCl	0.0000	0.0108	0.0000	0.0052	-0.16	-0.12	-0.16	-0.13	103.15 ± 0.02 [g]
Li_2	0.0000	0.0000	0.0000	0.0000	0.03	0.03	0.02	0.03	24.55 ± 0.79
LiF	0.0000	0.0042	0.0000	0.0028	-0.35	-0.33	-0.25	-0.33	138.50 ± 2.03
C_2H_2 (acetylene)	0.0000	0.0208	0.0000	0.0116	0.02	0.10	0.17	0.06	392.26 ± 0.24 [j]
C_2H_4 (ethylene)	0.0000	0.0208	0.0000	0.0116	-0.46	-0.37	-0.41	-0.41	538.50 ± 0.18 [d]
C_2H_6 (ethane)	0.0000	0.0208	0.0000	0.0116	-0.95	-0.86	-0.94	-0.91	675.29 ± 0.20 [f]
CN	0.3743	0.0183	0.0133	0.0102	1.97	0.57	1.31	0.88	178.98 ± 1.21 [f]
HCN	0.0000	0.0183	0.0000	0.0102	-0.43	-0.36	-0.20	-0.40	304.76 ± 0.96 [f]
CO	0.0000	0.0198	0.0000	0.0116	0.12	0.20	0.39	0.17	257.27 ± 0.13 [f]
HCO	0.0159	0.0198	0.0054	0.0116	0.03	0.05	0.36	0.02	272.96 ± 0.23 [d]
H_2CO	0.0000	0.0198	0.0000	0.0116	-0.38	-0.30	-0.15	-0.32	361.04 ± 0.17 [f]
CH_3OH	0.0000	0.0198	0.0000	0.0116	-0.61	-0.53	-0.52	-0.56	487.47 ± 0.13 [d]
N_2	0.0000	0.0158	0.0000	0.0088	0.40	0.47	0.64	0.44	225.83 ± 0.02 [k]
H_2NNH_2	0.0000	0.0158	0.0000	0.0088	-0.37	-0.31	-0.29	-0.34	411.49 ± 0.12 [f]
NO	0.0379	0.0173	0.0050	0.0102	0.68	0.59	0.92	0.57	150.86 ± 0.05 [d]
O_2	0.0487	0.0188	0.0131	0.0117	0.74	0.62	0.93	0.70	119.11 ± 0.03 [k]
HOOH	0.0000	0.0188	0.0000	0.0117	0.17	0.24	0.35	0.23	255.80 ± 0.06 [f]
F_2	0.3045	0.0084	0.0000	0.0056	1.72	0.56	1.04	0.91	37.95 ± 0.10 [k]
CO_2	0.0000	0.0292	0.0000	0.0175	-0.07	0.04	0.23	0.01	384.46 ± 0.13 [g]
Na_2	0.0000	0.0001	0.0000	0.0001	0.07	0.07	0.06	0.07	17.38 ± 0.05 [d]
Si_2	0.0293	0.0314	0.0083	0.0157	1.92	1.93	2.01	1.94	75.41 ± 3.16
P_2	0.0000	0.0014	0.0000	0.0009	1.08	1.08	1.27	1.19	116.87 ± 0.59 [g]
S_2	0.0622	0.0272	0.0162	0.0118	0.08	-0.05	0.12	0.01	101.76 ± 0.10 [g]
Cl_2	0.0000	0.0216	0.0000	0.0104	0.61	0.69	0.64	0.68	57.98 ± 0.00 [k]
NaCl	0.0000	0.0108	0.0000	0.0052	0.68	0.72	0.67	0.72	98.04 ± 0.53
SiO	0.0000	0.0251	0.0000	0.0137	1.27	1.37	1.61	1.35	191.75 ± 2.05

CS	0.0000	0.0240	0.0000	0.0117	1.08	1.17	1.33	1.15	170.65 ± 0.16 [d]
SO	0.0597	0.0230	0.0144	0.0118	0.94	0.80	1.10	0.72	124.61 ± 0.32
ClO	0.0203	0.0202	0.0081	0.0110	1.07	1.07	0.95	1.09	64.36 ± 0.50
FCl	0.0000	0.0150	0.0000	0.0080	0.13	0.19	0.26	0.19	61.17 ± 0.12
Si_2H_6	0.0000	0.0314	0.0000	0.0157	-1.65	-1.53	-1.67	-1.55	509.96 ± 0.62 [d]
CH_3Cl	0.0000	0.0212	0.0000	0.0110	-0.62	-0.54	-0.58	-0.57	376.19 ± 0.17 [d]
CH_3SH	0.0000	0.0240	0.0000	0.0117	-0.68	-0.59	-0.66	-0.61	451.42 ± 0.19 [l]
HOCl	0.0000	0.0202	0.0000	0.0110	-0.37	-0.29	-0.26	-0.30	158.46 ± 0.50
SO_2	0.0000	0.0324	0.0000	0.0176	1.06	1.19	1.37	1.18	256.25 ± 0.08 [d]
MD					0.01	0.00	0.07	0.00	
MAD					0.60	0.54	0.62	0.56	± 0.44
RMS					0.77	0.69	0.77	0.70	± 0.73
LD[m]					1.72 ± 0.10	1.19 ± 0.08	1.37 ± 0.08	-1.55 ± 0.62	
LD species					F_2	SO_2	SO_2	Si_2H_6	
Excluding species with experimental uncertainties > 0.24 kcal/mol									
MD					-0.03	-0.03	0.05	-0.03	
MAD					0.47	0.42	0.49	0.42	± 0.12
RMS					0.58	0.50	0.60	0.52	± 0.14
LD					1.72 ± 0.10	1.19 ± 0.08	1.37 ± 0.08	1.18 ± 0.08	
LD species					F_2	SO_2	SO_2	SO_2	

[a]The uncertainty in the calculated and experimental TAE value reflects the uncertainty in both the experimental atomic and molecular heats of formation.
[b]Experimental TAEs were calculated from experimental heats of formation of the atoms (Table S-I) and experimental heats of formation of the molecules (Table S-II). Unless otherwise noted, experimental heats of formation for the molecules are taken from Reference 11.
[c]Reference 12.
[d]Reference 9.
[e]M. Litorja. and B. Ruscic, J. Chem. Phys. **108**, 6748 (1998).
[f]Reference 13.
[g]Reference 10.
[h]B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, X. Qian, C. Ng, J. Liu, W. Chen, and D. W. Schwenke, J. Phys. Chem. A **106**, 2727 (2002).
[i]J. Berkowitz, J. P. Greene, H. Cho, and B. Ruscic, J. Chem. Phys. **86**, 1235 (1987).
[j]Reference 14.
[k]Standard state.
[l]W. D. Good, J. L. Lacina, J. P. McCullough, J. Phys. Chem. **65**, 2229 (1961).
[m]The choice of largest deviation (LD) for each method is not only determined by the magnitude of the deviation from experiment, but also by the experimental uncertainty itself. For example, the LD for W1U was selected to be 1.72 ± 0.10 kcal/mol (F_2) instead of 1.97 ± 1.21 kcal/mol (CN).

Table S-IV. Error in $\langle S^2 \rangle$ and deviation of total atomization energies (298 K, kcal/mol) from experiment for selected molecules from the G2-2 test set.[a]

	W1U $\Delta\langle S^2\rangle$		W1BD $\Delta\langle S^2\rangle$		Deviation (Expt. – Theory)				
Molecule	Reactant	Product	Reactant	Product	W1U	W1Usc	W1BD	W1RO	Experiment[b]
BF_3	0.0000	0.0239	0.0000	0.0139	0.0	0.1	0.1	0.1	465.8 ± 0.3 [c]
BCl_3	0.0000	0.0437	0.0000	0.0211	0.5	0.7	0.6	0.7	320.7 ± 0.5 [d]
CF_4	0.0000	0.0272	0.0000	0.0169	-1.4	-1.3	-1.2	-1.3	470.2 ± 0.3
OCS	0.0000	0.0334	0.0000	0.0176	0.3	0.4	0.5	0.4	331.0 ± 0.5
CS_2	0.0000	0.0376	0.0000	0.0176	0.3	0.5	0.5	0.4	275.8 ± 0.3 [e]
N_2O	0.0000	0.0252	0.0000	0.0146	0.7	0.8	1.1	0.8	265.8 ± 0.1 [e]
ClNO	0.0000	0.0281	0.0000	0.0154	1.7	1.8	2.0	1.8	188.9 ± 0.1
NF_3	0.0000	0.0205	0.0000	0.0128	0.1	0.2	0.4	0.2	201.4 ± 0.3 [d]
F_2O	0.0000	0.0178	0.0000	0.0114	1.1	1.1	1.4	1.1	91.6 ± 0.4
CH_2F_2	0.0000	0.0188	0.0000	0.0114	-0.6	-0.5	-0.4	-0.5	421.6 ± 0.3
CH_3CN	0.0000	0.0287	0.0000	0.0159	-0.2	-0.1	0.0	-0.1	594.1 ± 0.2 [f]
HCOOH	0.0000	0.0292	0.0000	0.0175	-0.3	-0.2	-0.1	-0.2	485.1 ± 0.2
C_2H_4O (oxirane)	0.0000	0.0302	0.0000	0.0174	-0.6	-0.5	-0.4	-0.5	623.1 ± 0.2 [e]
HCOCOH (glyoxal)	0.0000	0.0396	0.0000	0.0233	-0.5	-0.3	-0.1	-0.4	616.6 ± 0.3 [g]
CH_3OCH_3	0.0000	0.0302	0.0000	0.0174	-0.9	-0.8	-0.8	-0.8	758.8 ± 0.2 [g]
C_2H_5Cl	0.0000	0.0316	0.0000	0.0167	-0.8	-0.7	-0.8	-0.8	658.9 ± 0.3 [g]
CH_3COCH_3	0.0000	0.0406	0.0000	0.0232	-0.7	-0.6	-0.5	-0.6	938.0 ± 0.2 [e]
HS	0.0149	0.0136	0.0064	0.0059	-0.5	-0.5	-0.5	-0.4	84.2 ± 0.7 [h]
CCH	0.3545	0.0208	0.0282	0.0116	0.6	-0.7	0.2	0.0	258.8 ± 0.3 [i,j]
C_2H_3	0.1819	0.0208	0.0135	0.0116	-0.5	-1.2	-0.8	-0.8	427.3 ± 0.8 [e]
CH_3CO	0.0136	0.0302	0.0047	0.0174	-0.3	-0.2	0.0	-0.3	560.8 ± 0.3 [k]
CH_2OH (^2A)	0.0123	0.0198	0.0055	0.0116	-0.4	-0.4	-0.3	-0.4	391.3 ± 0.3 [e]
CH_3CH_2O	0.0106	0.0302	0.0062	0.0174	-0.2	-0.2	-0.2	-0.2	666.4 ± 0.8 [l]
CH_3S	0.0157	0.0240	0.0066	0.0117	-1.0	-1.0	-1.0	-1.0	364.1 ± 0.4 [l]
C_2H_5	0.0135	0.0208	0.0060	0.0116	-0.2	-0.1	-0.2	-0.2	574.7 ± 0.5 [m]
NO_2	0.0209	0.0267	0.0059	0.0161	1.1	1.1	1.5	1.0	223.8 ± 0.1
MD					-0.1	-0.1	0.0	-0.1	
MAD					0.6	0.6	0.6	0.6	± 0.2
RMS					0.7	0.7	0.8	0.7	± 0.2
LD (ClNO)					1.7 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	1.8 ± 0.1	±0.8

[a]Both atomic and molecular experimental uncertainties are included in the uncertainty for the deviation between experiment and theory. See Eq. (S.1). A separate error analysis, wherein species with experimental uncertainties > 0.24 kcal/mol are excluded, is not presented for Table S-IV since almost all members of this subset would fall under such category.
[b]Experimental TAEs were calculated from experimental heats of formation of the atoms (Table S-I) and experimental heats of formation of the molecules (Table S-II). Unless otherwise noted, experimental heats of formation for the molecules are taken from Reference 13.
[c]Reference 10.
[d]Reference 11.
[e]Reference 9.
[f]X. An, M. Mansson, J. Chem. Thermodyn. **15**, 287 (1983).
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[i]D. H. Mordaunt and M. N. R. Ashfold, J. Chem. Phys. **101**, 2630 (1994)
[j]Reference 14.

[k]J. T. Niiranen, D. Gutman, and L. N. Krasnoperov, J. Phys. Chem. **96**, 5881 (1992); C. W. Bauschlicher, Jr., J. Phys. Chem. **98**, 2564 (1994).
[l]J. Berkowitz, G. B. Ellison, and D. Gutman, J. Phys. Chem. **98**, 2744 (1994) and references therein.
[m]W. Tsang, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman (Blackie Academic and Professional, London, 1996).

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III. Electron affinities, ionization potentials, and proton affinities

The adiabatic electron affinities are calculated as the difference in total energies at 0 K between the neutral species and its anion, while the adiabatic ionization potentials are obtained as the difference in total energies at 0 K between the cation and neutral. Proton affinities are calculated as the difference in total energies at 0 K between the neutral species and its protonated form. For comparison of PAs with experimental values at 298 K, thermal corrections were obtained at the B3LYP/cc-pVTZ+1*d* level, with the enthalpy function, $\frac{5}{2}RT$, employed as the correction for the H^+ ion. These values were then added onto the computed W1U, W1Usc, W1BD, and W1(RO) PAs at 0 K.

The error in the calculated chemical energy differences (Experiment – Theory, kcal/mol) are presented in Tables S-V and S-VI for the EAs, in Tables S-VII and S-VIII for the IPs, and in Table S-IX for the PAs. The error in $\langle S^2 \rangle$ is also included in Tables S-V, S-VI, S-VII, and S-VIII.

Table S-V. Error in $\langle S^2 \rangle$ and deviation of electron affinities (kcal/mol) from experiment of the G2-1 test set.[a]

	W1U $\Delta\langle S^2\rangle$		W1BD $\Delta\langle S^2\rangle$		Deviation (Expt – Theory)				
Molecule	Reactant	Product	Reactant	Product	W1U	W1Usc	W1BD	W1RO	Experiment[a]
C	0.0069	0.0104	0.0037	0.0058	0.23	0.25	0.27	0.25	29.12±0.01 [b]
O	0.0210	0.0094	0.0097	0.0059	0.39	0.34	0.53	0.35	33.69±0.00 [b]
F	0.0000	0.0042	0.0000	0.0028	-0.22	-0.20	-0.09	-0.20	78.43±0.00 [b]
Si	0.0008	0.0157	0.0002	0.0079	0.25	0.31	0.22	0.26	32.04±0.00 [c]
P	0.0272	0.0007	0.0129	0.0004	0.28	0.18	0.25	0.29	17.21±0.01 [b]
S	0.0140	0.0136	0.0070	0.0059	-0.07	-0.07	-0.09	-0.05	47.90±0.00 [b]
Cl	0.0000	0.0108	0.0000	0.0052	-0.39	-0.34	-0.39	-0.35	83.31±0.00 [b]
CH	0.0240	0.0098	0.0108	0.0048	0.76	0.71	0.77	0.74	28.55±0.18
CH_2 ($^3B_1$)	0.0190	0.0168	0.0072	0.0081	0.27	0.26	0.30	0.25	15.04±0.14
CH_3	0.0000	0.0118	0.0000	0.0054	1.17	1.22	1.19	1.19	1.84±0.69
NH	0.0868	0.0168	0.0117	0.0086	0.64	0.37	0.62	0.50	8.53±0.09
NH_2	0.0000	0.0098	0.0000	0.0049	0.42	0.46	0.50	0.45	17.90±0.85
OH	0.0000	0.0072	0.0000	0.0041	0.07	0.10	0.20	0.10	42.15±0.00
SiH	0.0375	0.0239	0.0096	0.0080	0.79	0.74	0.74	0.76	29.45±0.20
SiH_2 ($^1A_1$)	0.0266	0.0000	0.0078	0.0000	1.04	0.94	1.00	1.00	25.90±0.51
SiH_3	0.0000	0.0052	0.0000	0.0032	0.17	0.19	0.16	0.19	32.42±0.32
PH	0.0228	0.0291	0.0084	0.0095	0.16	0.19	0.12	0.18	23.71±0.23
PH_2	0.0000	0.0207	0.0000	0.0076	0.21	0.29	0.18	0.25	29.31±0.23
SH	0.0000	0.0149	0.0000	0.0064	-0.12	-0.06	-0.13	-0.07	53.43±0.05
O_2	0.0454	0.0487	0.0087	0.0131	0.21	0.23	0.27	0.23	10.40±0.16
NO	0.0530	0.0379	0.0159	0.0050	-0.09	-0.14	-0.16	-0.12	0.60±0.12
CN	0.0000	0.3743	0.0000	0.0133	-1.79	-0.31	-0.96	-0.66	89.06±0.12
PO	0.0456	0.0230	0.0116	0.0076	0.05	-0.04	-0.12	-0.04	25.18±0.23
S_2	0.0358	0.0622	0.0095	0.0162	-0.67	-0.56	-0.72	-0.60	38.35±0.92
Cl_2	0.0251	0.0000	0.0091	0.0000	-0.44	-0.54	-0.49	-0.55	54.88±2.31 [d]
MD					0.14	0.18	0.17	0.17	
MAD					0.44	0.36	0.42	0.39	±0.11
RMS					0.60	0.46	0.52	0.49	±0.11
LD					-1.79	1.22	1.19	1.19	
LD species					CN	CH_3	CH_3	CH_3	
Excluding species with experimental uncertainties > 0.24 kcal/mol									
MD					0.09	0.15	0.13	0.14	
MAD					0.37	0.27	0.34	0.30	±0.09
RMS					0.54	0.33	0.42	0.37	±0.09
LD					-1.79	0.74	-0.96	0.76	
LD species					CN	SiH	CN	SiH	

[a]From Reference 15 unless otherwise noted.
[b]Reference 16.
[c]J. Thogersen, L. D. Steele, M. Scheer, C. A. Brodie, and H. K. Haugen, J. Phys. B **29**, 1323 (1996).
[d]M. K. Gilles, M. L. Polak, and W. C. Lineberger, J. Chem. Phys. **96**, 8012 (1992).

Table S-VI. Error in $\langle S^2 \rangle$ and deviation of electron affinities (kcal/mol) from experiment of the G2-2 test set.[a]

	W1U Δ<S²>		W1BD Δ<S²>		Deviation (Expt. – Theory)				
Molecule	Reactant	Product	Reactant	Product	W1U	W1Usc	W1BD	W1RO	Experiment[a]
Li	0.0000	0.0000	0.0000	0.0000	-0.02	-0.02	-0.03	-0.02	14.24±0.01
B	0.0095	0.0113	0.0050	0.0056	0.49	0.50	0.47	0.49	6.45±0.00 [b]
Na	0.0000	0.0001	0.0000	0.0001	-0.06	-0.06	-0.06	-0.06	12.64±0.00
Al	0.0181	0.0206	0.0072	0.0086	0.48	0.49	0.45	0.46	9.98±0.00 [c]
C_2	0.0204	1.6059	0.0057	0.5622	-2.64	-2.11	-0.41	0.29	75.48±0.18
C_2O	0.0306	0.0592	0.0080	0.0150	-0.52	-0.40	-0.55	-0.36	52.79±0.42
CF_2	0.0221	0.0000	0.0080	0.0000	0.51	0.42	0.56	0.43	4.13±0.12
NCO	0.0000	0.0945	0.0000	0.0161	-0.76	-0.39	-0.72	-0.51	83.23±0.12
NO_2	0.0000	0.0209	0.0000	0.0059	-0.47	-0.39	-0.54	-0.32	52.42±0.12
O_3	0.0351	0.9418	0.0072	0.2059	-7.80	-4.23	-3.96	-1.53	48.50±0.09
OF	0.0000	0.0190	0.0000	0.0054	-1.03	-0.96	-0.66	-0.95	52.39±0.14
SO_2	0.0352	0.0000	0.0087	0.0000	-0.55	-0.69	-0.64	-0.71	25.53±0.18
S_2O	0.0369	0.0000	0.0094	0.0000	-0.30	-0.45	-0.54	-0.53	43.29±0.18
CCH	0.0000	0.3545	0.0000	0.0282	-0.42	0.98	0.10	0.22	68.47±0.14
C_2H_3	0.0000	0.1819	0.0000	0.0135	-0.48	0.24	-0.19	-0.15	15.38±0.55
CH_2CC	0.1468	0.0000	0.0212	0.0000	-0.19	-0.77	-0.43	-0.56	41.37±0.18
CH_2CCH	0.0000	0.2062	0.0000	0.0264	-0.70	0.11	-0.44	-0.34	20.59±0.12
CH_2CHCH_2	0.0000	0.1993	0.0000	0.0415	-0.53	0.25	-0.31	-0.09	11.09±0.18
HCO	0.0000	0.0159	0.0000	0.0054	0.51	0.58	0.39	0.58	7.22±0.18
HCF	0.0205	0.0000	0.0074	0.0000	0.14	0.06	0.17	0.08	12.50±0.12
CH_3O	0.0000	0.0105	0.0000	0.0059	0.26	0.31	0.41	0.30	36.21±0.12
CH_3S	0.0000	0.0157	0.0000	0.0066	-0.28	-0.22	-0.27	-0.23	42.92±0.09
CH_2S	0.0301	0.0000	0.0093	0.0000	-0.89	-1.01	-1.08	-0.99	10.72±0.53
CH_2CN	0.0000	0.1861	0.0000	0.0206	-0.38	0.36	-0.11	-0.04	35.61±0.14 [d]
CH_2NC	0.0000	0.0824	0.0000	0.0157	-1.96	-1.64	-1.81	-1.74	24.40±0.60 [d]
CHCO	0.0000	0.0649	0.0000	0.0116	0.54	0.79	0.53	0.75	54.19±0.51
CH_2CHO	0.0000	0.1734	0.0000	0.0222	-0.58	0.10	-0.30	-0.20	42.07±0.00
CH_3CO	0.0000	0.0136	0.0000	0.0047	0.54	0.60	0.46	0.61	9.75±0.85
CH_3CH_2O	0.0000	0.0106	0.0000	0.0062	0.56	0.61	0.72	0.60	39.50±0.12
LiH	0.0004	0.0000	0.0003	0.0000	0.19	0.19	0.18	0.19	7.89±0.28
HNO	0.0383	0.0000	0.0085	0.0000	0.16	0.01	0.07	0.05	7.79±0.35
HO_2	0.0000	0.0135	0.0000	0.0060	-0.08	-0.03	0.21	-0.04	24.86±0.39
MD					-0.51	-0.08	-0.26	-0.13	
MAD					0.78	0.62	0.56	0.45	±0.05
RMS					1.57	1.01	0.89	0.60	±0.05
LD					-7.80	-4.23	-3.96	-1.74	
LD species					O_3	O_3	O_3	CH_2NC	
Excluding C_2 and O_3									
MD					-0.19	-0.01	-0.13	-0.10	
MAD					0.49	0.45	0.45	0.42	±0.06
RMS					0.61	0.58	0.57	0.55	±0.06
LD (CH_2NC)					-1.96	-1.64	-1.81	-1.74	

Excluding C_2, O_3, and species with experimental uncertainties > 0.24 kcal/mol					
MD	-0.17	0.02	-0.11	-0.08	
MAD	0.44	0.41	0.40	0.37	±0.03
RMS	0.50	0.49	0.45	0.44	±0.03
LD	-1.03	0.98	±0.72	-0.95	
LD species	OF	CCH	CH_3CH_2O/ NCO	OF	

[a]From Reference 15 unless otherwise noted.
[b]M. Scheer, R. C. Bilodeau, and H. K. Haugen, Phys. Rev. Lett. **80**, 2562 (1998).
[c]M. Scheer, R. C. Bilodeau, J. Thogersen, and H. K. Haugen, Phys. Rev. A **57**, 1493 (1998).
[d]J. Berkowitz, G. B. Ellison, and D. Gutman, J. Phys. Chem. **98**, 2744 (1994).

Table S-VII. Error in $\langle S^2 \rangle$ and deviation of ionization potentials (kcal/mol) from experiment of the G2-1 test set.[a]

	W1U $\Delta\langle S^2\rangle$		W1BD $\Delta\langle S^2\rangle$		Deviation (Expt – Theory)				Experiment[a]
Species	Reactant	Product	Reactant	Product	W1U	W1Usc	W1BD	W1RO	
Li	0.0000	0.0000	0.0000	0.0000	0.12	0.12	0.12	0.12	124.34± 0.00
Be	0.0000	0.0000	0.0000	0.0000	0.03	0.03	0.01	0.03	214.99±0.00
B	0.0113	0.0000	0.0056	0.0000	0.45	0.41	0.46	0.43	191.36±0.00
C	0.0104	0.0067	0.0058	0.0039	0.28	0.26	0.27	0.27	259.67±0.00
N	0.0079	0.0070	0.0044	0.0043	0.11	0.10	0.10	0.11	335.17±0.02
O	0.0094	0.0056	0.0059	0.0034	0.46	0.44	0.47	0.44	314.04±0.02
F	0.0042	0.0053	0.0028	0.0036	0.29	0.29	0.32	0.29	401.79±0.02
Na	0.0001	0.0000	0.0001	0.0000	0.19	0.19	0.20	0.19	118.51±0.02
Mg	0.0000	0.0001	0.0000	0.0001	0.31	0.31	0.30	0.31	176.32±0.02
Al	0.0206	0.0000	0.0086	0.0000	0.59	0.51	0.60	0.56	138.04±0.02
Si	0.0157	0.0166	0.0079	0.0078	0.51	0.51	0.50	0.49	187.99±0.00
P	0.0007	0.0135	0.0004	0.0073	0.35	0.40	0.33	0.35	241.83±0.00
S	0.0136	0.0009	0.0059	0.0005	0.37	0.32	0.36	0.38	238.91±0.02
Cl	0.0108	0.0115	0.0052	0.0050	0.08	0.08	0.06	0.10	299.04±0.00
CH_4 (C_{2v})	0.0000	0.0073	0.0000	0.0038	0.15	0.18	0.14	0.17	290.80±0.23
NH_3	0.0000	0.0114	0.0000	0.0055	0.05	0.09	0.06	0.07	234.90±0.00[b]
OH	0.0072	0.0146	0.0041	0.0078	0.04	0.07	0.07	0.04	300.19±0.00
H_2O	0.0000	0.0081	0.0000	0.0043	0.02	0.06	0.06	0.05	291.08±0.01
FH	0.0000	0.0052	0.0000	0.0032	-1.01	-0.98	-0.96	-0.99	369.99±0.07
SiH_4	0.0000	0.0045	0.0000	0.0027	-0.10	-0.08	-0.09	-0.08	253.67±0.46
PH	0.0291	0.0179	0.0095	0.0073	-0.05	-0.09	-0.08	-0.08	234.05±0.18
PH_2	0.0207	0.0000	0.0076	0.0000	0.14	0.06	0.11	0.09	226.55±0.05
PH_3	0.0000	0.0078	0.0000	0.0043	-0.08	-0.05	-0.08	-0.06	227.61±0.05
HS	0.0149	0.0224	0.0064	0.0089	0.15	0.18	0.13	0.17	240.34±0.01
H_2S ($^2B_1$)	0.0000	0.0167	0.0000	0.0071	-0.27	-0.20	-0.28	-0.23	241.06±0.02
H_2S ($^2A_1$)	0.0000	0.0161	0.0000	0.0058	-0.14	-0.08	-0.13	-0.09	294.26±0.83
HCl[a]	0.0000	0.0123	0.0000	0.0058	-0.03	0.02	-0.04	0.00	293.93±0.00
C_2H_2	0.0000	0.0051	0.0000	0.0028	-0.04	-0.02	-0.01	-0.02	262.96±0.01
C_2H_4	0.0000	0.0051	0.0000	0.0028	-0.17	-0.15	-0.15	-0.16	242.46±0.01
CO	0.0000	0.2084	0.0000	0.0189	-0.91	-0.09	-0.55	-0.18	323.18±0.01
N_2 $^2\Sigma$	0.0000	0.0177	0.0000	0.0050	-1.04	-0.97	-1.48	-1.03	359.31±0.18
N_2 $^2\pi$	0.0000	0.0033	0.0000	0.0020	-0.33	-0.31	-0.32	-0.30	385.10±0.02
O_2	0.0487	0.0131	0.0131	0.0040	-0.35	-0.49	-0.52	-0.42	278.34±0.00
P_2	0.0000	0.0093	0.0000	0.0042	1.36	1.39	1.40	1.42	243.69±0.05
S_2	0.0622	0.0317	0.0162	0.0083	-0.16	-0.28	-0.31	-0.24	215.76±0.05
Cl_2	0.0000	0.0271	0.0000	0.0078	-0.55	-0.44	-0.59	-0.47	264.76±0.07
ClF	0.0000	0.0147	0.0000	0.0061	-0.10	-0.04	-0.18	-0.03	291.95±0.23
CS	0.0000	0.7098	0.0000	0.0424	-2.10	0.70	-0.62	-0.34	261.28±0.23
MD					-0.04	0.06	-0.01	0.04	
MAD					0.35	0.29	0.33	0.28	±0.17
RMS					0.55	0.42	0.47	0.41	±0.17
LD					-2.10	1.39	-1.48	1.42	
LD species					CS	P_2	N_2 $^2\Sigma$	P_2	

Excluding species with experimental uncertainties > 0.24 kcal/mol

MD	-0.03	0.07	0.00	0.04	
MAD	0.37	0.30	0.34	0.29	±0.08
RMS	0.57	0.43	0.48	0.42	±0.08
LD	-2.10	1.39	-1.48	1.42	
LD species	CS	P_2	N_2 $^2\Sigma$	P_2	

[a]From Reference 15 unless otherwise noted.
[b]R. Seiler, U. Hollenstein, T. P. Softley, and F. Merkt, J. Chem. Phys. **118**, 10024 (2003).

Table S-VIII. Error in $\langle S^2 \rangle$ and deviation of ionization potentials (kcal/mol) from experiment of the G2-2 test set.[a]

	W1U $\Delta\langle S^2\rangle$		W1BD $\Delta\langle S^2\rangle$		Deviation (Expt – Theory)				
Species	Reactant	Product	Reactant	Product	W1U	W1Usc	W1BD	W1RO	Experiment[a]
H	0.0000	0.0000	0.0000	0.0000	-0.14	-0.14	-0.14	-0.14	313.61±0.02
He	0.0000	0.0000	0.0000	0.0000	0.01	0.01	0.01	0.01	567.02±0.02
Ne	0.0000	0.0027	0.0000	0.0019	-0.29	-0.28	-0.25	-0.27	497.31±0.02
Ar	0.0000	0.0094	0.0000	0.0046	-0.15	-0.12	-0.17	-0.12	363.44±0.02
BF_3[b]	0.0000	0.0378	0.0000	0.0099	-0.71	-0.56	-0.80	-0.59	362.29±2.31
CO_2	0.0000	0.2215	0.0000	0.0340	-1.18	-0.31	-1.12	-0.77	317.73±0.05
CF_2	0.0000	0.0058	0.0000	0.0038	-0.24	-0.22	-0.38	-0.22	263.36±0.23
OCS	0.0000	0.0766	0.0000	0.0105	-0.11	0.19	-0.05	0.12	257.94±0.05
CS_2	0.0000	0.2847	0.0000	0.0433	-0.75	0.37	-0.35	-0.09	232.45±0.05
CH_2	0.0168	0.0062	0.0081	0.0033	0.54	0.50	0.52	0.53	239.74±0.07
CH_3	0.0118	0.0000	0.0054	0.0000	-0.06	-0.10	-0.07	-0.08	226.85±0.12
C_2H_5 ($^2A'$)	0.0135	0.0000	0.0060	0.0000	-0.18	-0.23	-0.22	-0.21	187.19±0.18
C_3H_4 (cyclopropene)	0.0000	0.0120	0.0000	0.0053	-0.18	-0.13	-0.06	0.55	222.95±0.12
CH_2CCH_2	0.0000	0.1038	0.0000	0.0145	-0.68	-0.27	-0.55	-0.43	223.41±0.05
sec-C_3H_7	0.0147	0.0000	0.0064	0.0000	-1.77	-1.82	-1.80	-1.82	169.96±0.46
C_6H_6	0.0000	0.0778	0.0000	0.0184	-0.68	-0.37	-0.62	-0.45	213.17±0.00
CN ($^3\Pi$)[c]	0.3743	0.2642	0.0133	0.0073	-0.64	-1.07	-0.89	-0.91	323.55±0.46
CN ($^1\Sigma^+$)[c]	0.3743	0.0000	0.0133	0.0000	4.86	3.39	1.05	3.74	323.55±0.46
CHO	0.0159	0.0000	0.0054	0.0000	-0.17	-0.23	-0.28	-0.24	187.72±0.92
CH_2OH (^2A)	0.0123	0.0000	0.0055	0.0000	0.38	0.33	0.23	0.34	174.34±0.23
CH_3O ($^2A'$)	0.0105	0.0350	0.0059	0.0174	-0.22	-0.12	-0.17	-0.17	247.21±0.23
CH_3OH	0.0000	0.0179	0.0000	0.0083	-0.84	-0.77	-0.53	-0.82	250.21±0.69
CH_3F	0.0000	0.0125	0.0000	0.0057	-0.59	-0.54	-0.69	-0.54	289.18±0.23
CH_2S	0.0000	0.1971	0.0000	0.0147	-0.70	0.08	-0.36	-0.30	216.22±0.07
CH_2SH	0.0220	0.0000	0.0086	0.0000	-0.57	-0.65	-0.76	-0.63	173.79±0.07
CH_3SH	0.0000	0.0177	0.0000	0.0073	-0.23	-0.16	-0.21	-0.17	217.77±0.05
CH_3Cl	0.0000	0.0134	0.0000	0.0063	-0.55	-0.50	-0.46	-0.50	259.78±0.07
CH_3CHO	0.0000	0.0268	0.0000	0.0102	-0.81	-0.71	-0.58	-0.73	235.84±0.12
CH_3OF[d]	0.0000	0.0503	0.0000	0.0070	-1.03	-0.84	-0.69	-0.86	261.51±0.18
C_2H_4S (thiirane)	0.0000	0.0189	0.0000	0.0080	-0.36	-0.29	-0.35	-0.29	208.73±0.14
NCCN	0.0000	0.3483	0.0000	0.0342	-1.79	-0.42	-1.26	-1.01	308.42±0.18
C_4H_4O (furan)	0.0000	0.0644	0.0000	0.0147	0.12	0.37	0.13	0.30	205.47±0.23
B_2H_4	0.0000	0.0060	0.0000	0.0032	2.93	2.96	2.94	2.95	223.69±0.46
NH	0.0168	0.0071	0.0086	0.0039	0.46	0.42	0.45	0.45	311.09±0.23
NH_2	0.0098	0.0241	0.0049	0.0117	-0.74	-0.68	-0.72	-0.74	256.90±0.23
N_2H_2	0.0000	0.0137	0.0000	0.0042	-0.26	-0.21	-0.34	-0.23	221.13±0.16
N_2H_3	0.0172	0.0000	0.0069	0.0000	-0.06	-0.13	-0.23	-0.12	175.49±0.23
HOF	0.0000	0.0218	0.0000	0.0057	-0.57	-0.49	-0.40	-0.50	293.11±0.23
SiH_2 ($^1A_1$)	0.0000	0.0064	0.0000	0.0034	0.36	0.39	0.36	0.38	211.01±0.46
SiH_3	0.0052	0.0000	0.0032	0.0000	0.51	0.49	0.49	0.49	187.60±0.12
Si_2H_2	0.0000	0.0862	0.0000	0.0166	0.07	0.41	0.13	0.19	189.10±0.46
Si_2H_4	0.0000	0.0115	0.0000	0.0047	0.65	0.70	0.67	0.69	186.56±0.69
Si_2H_6	0.0000	0.0061	0.0000	0.0036	2.13	2.15	2.14	2.14	224.61±0.46
MD					-0.21	-0.05	-0.16	-0.10	
MAD					0.60	0.50	0.55	0.54	±0.47
RMS					0.85	0.75	0.80	0.78	±0.47
LD (B_2H_4)					2.93	2.96	2.94	2.95	

Excluding B_2H_4, sec-C_3H_7, and Si_2H_6[b]					
MD	-0.31	-0.14	-0.26	-0.19	
MAD	0.47	0.36	0.42	0.40	±0.08
RMS	0.60	0.42	0.50	0.47	±0.08
LD	-1.79	-0.84	-1.26	-1.01	
LD species	NCCN	CH_3OF	NCCN	NCCN	
Excluding B_2H_4, sec-C_3H_7, Si_2H_6, and species with experimental uncertainties > 0.24 kcal/mol					
MD	-0.35	-0.16	-0.29	-0.21	
MAD	0.47	0.33	0.41	0.39	±0.03
RMS	0.60	0.39	0.50	0.46	±0.03
LD	-1.79	-0.84	-1.26	-1.01	
LD species	NCCN	CH_3OF	NCCN	NCCN	

[a]From Reference 15 unless otherwise noted.
[b]Excluded in error statistics of original W1(RO) study (see reference 7).

Table S-IX. Deviation of proton affinities (298 K, kcal/mol) from experiment.

	Deviation (Expt. – Theory)			
Molecule	W1U	W1BD	W1(RO)	Experiment[a]
NH_3	-0.04	-0.05	-0.03	204.02
H_2O	0.18	0.16	0.18	165.15
C_2H_2	-0.83	-0.88	-0.83	153.30
SiH_4	-0.36	-0.35	-0.36	152.89
PH_3	0.39	0.40	0.41	187.62
H_2S	-0.56	-0.54	-0.56	168.50
HCl	-0.63	-0.62	-0.63	133.10
H_2	-0.38	-0.39	-0.38	100.93
MD	-0.28	-0.28	-0.28	
MAD	0.42	0.42	0.42	
RMS	0.48	0.49	0.48	
LD (C_2H_2)	-0.83	-0.88	-0.83	

[a]Reference 17.

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