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Bond Dissociation Energies and Radical Stabilization Energies: An Assessment of Contemporary Theoretical Procedures — Source link

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ADDITIONS AND CORRECTIONS

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Ambili S. Menon, Geoffrey P. F. Wood, Damian Moran and Leo Radom*:

Correction to "Bond Dissociation Energies and Radical Stabilization Energies: An Assessment of Contemporary Theoretical Procedures"

SUPPORTING INFORMATION

(Tables S1, S2 and S3. Total 10 Pages)

TABLE S1: Total Energies of Substituted Methyl Radicals (•CH_2X) and Substituted Methanes (CH_3X) (0 K, Hartrees)[a]

Species	UBMK[a,b]	RBMK[a,b]	UMPWB1K[a,b]	RMPWB1K[a,b]	UM05[a,b]	UM05-2X[a,b]	UB2-PLYP[a,b]	RB2-PLYP[a,b]	UMPW2-PLYP[a,b]	RMPW2-PLYP[a,b]	G3(MP2)-RAD	G3X(MP2)-RAD	CBS-QB3	ROCBS-QB3	W1[c]
CH_4	–40.44822	–40.44822	–40.45075	–40.45075	–40.44193	–40.47154	–40.44556	–40.44556	–40.44437	–40.44437	–40.42078	–40.42170	–40.40999	–40.40999	–40.47905
•CH_3	–39.78558	–39.78402	–39.78902	–39.78751	–39.78223	–39.80941	–39.78573	–39.78428	–39.78479	–39.78328	–39.75592	–39.75649	–39.74479	–39.74510	–39.81440
CH_3NH_2	–95.76173	–95.76173	–95.76726	–95.76726	–95.75146	–95.80951	–95.75473	–95.75474	–95.75266	–95.75266	–95.68517	–95.68653	–95.66847	–95.66847	–95.82950
•CH_2NH_2	–95.11970	–95.11823	–95.12629	–95.12469	–95.11139	–95.16701	–95.11456	–95.11321	–95.11256	–95.11108	–95.03716	–95.03853	–95.02214	–95.02244	–95.18362
CH_3OH	–115.64707	–115.64707	–115.65165	–115.65165	–115.64256	–115.69557	–115.63858	–115.63858	–115.63610	–115.63610	–115.55178	–115.55304	–115.53995	–115.53995	–115.73250
•CH_2OH	–114.99933	–114.99790	–115.00488	–115.00330	–114.99679	–115.04691	–114.99269	–114.99134	–114.99027	–114.98881	–114.89894	–114.90019	–114.88814	–114.88835	–115.08129
CH_3OCH_3	–154.90282	–154.90282	–154.91164	–154.91164	–154.89179	–154.97448	–154.89058	–154.89059	–154.88811	–154.88811	–154.77068	–154.77276	–154.75222	–154.75222	–155.01220
•CH_2OCH_3	–154.25518	–154.25378	–154.26414	–154.26318	–154.24603	–154.32563	–154.24482	–154.24351	–154.24233	–154.24089	–154.11764	–154.11972	–154.10026	–154.10047	–154.36094
CH_3F	–139.68541	–139.68541	–139.69377	–139.69377	–139.68761	–139.73578	–139.67463	–139.67463	–139.67259	–139.67259	–139.56943	–139.57075	–139.56384	–139.56384	–139.80024
•CH_2F	–139.02900	–139.02762	–139.03871	–139.03728	–139.03357	–139.07880	–139.02072	–139.01936	–139.01877	–139.01732	–138.90931	–138.91052	–138.90421	–138.90445	–139.14121
CH_3CH_3	–79.71196	–79.71196	–79.71970	–79.71970	–79.69961	–79.75857	–79.70585	–79.70585	–79.70452	–79.70452	–79.64934	–79.65086	–79.63057	–79.63057	–79.76918
•CH_2CH_3	–79.05598	–79.05429	–79.06523	–79.06363	–79.04850	–79.10309	–79.05262	–79.05113	–79.05149	–79.04990	–78.98986	–78.99118	–78.97155	–78.97183	–79.11056
$CH_3CH_2CH_3$	–118.97936	–118.97936	–118.99225	–118.99225	–118.96074	–119.05003	–118.97009	–118.97010	–118.96873	–118.96873	–118.88265	–118.88479	–118.85587	–118.85587	–119.06372
•$CH_2CH_2CH_3$	–118.32224	–118.32058	–118.33626	–118.33479	–118.30830	–118.39330	–118.31568	–118.31423	–118.31444	–118.31290	–118.22255	–118.22385	–118.19574	–118.19603	–118.40391
CH_3CF_3	–377.49224	–377.49224	–377.52005	–377.52005	–377.50841	–377.62048	–377.46247	–377.46247	–377.45921	–377.45921	–377.16617	–377.16322	–377.16323	–377.16323	–377.80356
•CH_2CF_3	–376.82736	–376.82574	–376.85626	–376.85514	–376.84858	–376.95619	–376.80107	–376.79961	–376.79787	–376.79634	–376.49835	–376.49584	–376.49553	–376.49584	–377.13658
$CH_3CF_2CF_3$	–615.26224	–615.26224	–615.30796	–615.30796	–615.29107	–615.46947	–615.21419	–615.21418	–615.20958	–615.20958	–614.72789	–614.73353	–614.72754	–614.72754	
•$CH_2CF_2CF_3$	–614.59869	–614.59706	–614.64518	–614.64428	–614.63237	–614.80631	–614.55390	–614.55245	–614.54936	–614.54783	–614.06114	–614.06676	–614.06114	–614.02598	
CH_3PH_2	–382.30044	–382.30044	–382.43598	–382.43598	–382.39051	–382.40920	–382.31254	–382.31254	–382.31964	–382.31964	–381.92725	–381.92933	–381.90707	–381.90707	–383.05162[c]

•CH_2PH_2	–381.64959	–381.64776	–381.78600	–381.78403	–381.74365	–381.75778	–381.66364	–381.66197	–381.67090	–381.66907	–381.27125	–381.27322	–381.25270	–381.25267	–382.39723 [c]
CH_3SH	–438.53833	–438.53833	–438.70251	–438.70251	–438.65156	–438.66601	–438.56527	–438.56527	–438.57282	–438.57282	–438.16994	–438.17188	–438.15282	–438.15282	–439.57214 [c]
•CH_2SH	–437.89014	–437.88837	–438.05731	–438.05533	–438.00855	–438.01929	–437.92099	–437.91943	–437.92859	–437.92685	–437.51884	–437.52087	–437.50337	–437.50351	–438.92326 [c]
CH_3Cl	–499.94444	–499.94444	–500.13322	–500.13322	–500.07758	–500.08375	–499.96290	–499.96290	–499.97282	–499.97282	–499.57329	–499.57502	–499.56208	–499.56208	–501.31991 [c]
•CH_2Cl	–499.28969	–499.28794	–499.48153	–499.47973	–499.42820	–499.43036	–499.31191	–499.31035	–499.32193	–499.32024	–498.91647	–498.91832	–498.90592	–498.90605	–500.66404 [c]
CH_3Br	–2612.67435	–2612.67435	–2614.33712	–2614.33712	–2613.92922	–2613.96091	–2613.68177	–2613.68177	–2613.71474	–2613.71474			–2612.68925		
•CH_2Br	–2612.01850	–2612.01672	–2613.68321	–2613.68137	–2613.27816	–2613.30400	–2613.02840	–2613.02689	–2613.06149	–2613.05984			–2612.02790		
CH_3BH_2	–65.85100	–65.85100	–65.85383	–65.85383	–65.84045	–65.88878	–65.84313	–65.84313	–65.84237	–65.84237	–65.78322	–65.78438	–65.76609	–65.76609	–65.89024
•CH_2BH_2	–65.20658	–65.20539	–65.20897	–65.20799	–65.19736	–65.24295	–65.19959	–65.19856	–65.19904	–65.19796	–65.13362	–65.13473	–65.11716	–65.11705	–65.24117
$CH_3CH{=}CH_2$	–117.77224	–117.77224	–117.78653	–117.78653	–117.75395	–117.84280	–117.76751	–117.76751	–117.76541	–117.76541	–117.67130	–117.67293	–117.64621	–117.64621	–117.85362
•$CH_2CH{=}CH_2$	–117.13801	–117.13340	–117.15419	–117.14894	–117.12668	–117.20979	–117.13503	–117.13309	–117.13334	–117.13060	–117.03337	–117.03480	–117.00950	–117.00964	–117.21574
$CH_3C{\equiv}CH$	–116.54903	–116.54903	–116.56475	–116.56475	–116.53654	–116.61915	–116.55048	–116.55048	–116.54733	–116.54733	–116.44388	–116.44525	–116.42172	–116.42172	–116.62846
•$CH_2C{\equiv}CH$	–115.90894	–115.90503	–115.92655	–115.92221	–115.90264	–115.97946	–115.91192	–115.91070	–115.90903	–115.90717	–115.79906	–115.80019	–115.77866	–115.77819	–115.98424
$CH_3C_6H_5$	–271.32470	–271.32470	–271.36758	–271.36758	–271.28053	–271.48964	–271.31867	–271.31867	–271.31476	–271.31476	–271.06697	–271.07059	–271.02044	–271.02044	–271.50079
•$CH_2C_6H_5$	–270.68578	–270.68216	–270.73004	–270.72603	–270.64828	–270.85116	–270.67959	–270.67960	–270.67615	–270.67540	–270.42454	–270.42793	–270.37807	–270.37961	–270.85866
CH_3CHO	–153.73818	–153.73818	–153.74591	–153.74591	–153.72996	–153.80379	–153.72867	–153.72867	–153.72515	–153.72515	–153.59909	–153.60054	–153.58247	–153.58247	–153.84286
•CH_2CHO	–153.09103	–153.08764	–153.10055	–153.09670	–153.08663	–153.15759	–153.08285	–153.08191	–153.07970	–153.07820	–152.94754	–152.94904	–152.93284	–152.93225	–153.19213
CH_3COOH	–228.99069	–228.99069	–229.00088	–229.00088	–228.98531	–229.08121	–228.97474	–228.97474	–228.97006	–228.97006	–228.78232	–228.78436	–228.76536	–228.76536	–229.14894
•CH_2COOH	–228.33771	–228.33563	–228.34929	–228.34730	–228.33706	–228.42910	–228.32453	–228.32322	–228.32001	–228.31850	–228.12552	–228.12757	–228.10974	–228.10962	–228.49331
CH_3COOCH_3	–268.24512	–268.24512	–268.25947	–268.25947	–268.23227	–268.35930	–268.22568	–268.22568	–268.22093	–268.22093	–268.00079	–268.00355	–267.97707	–267.97707	–268.42797
•CH_2COOCH_3	–267.59225	–267.59024	–267.60795	–267.60610	–267.58430	–267.70726	–267.57568	–267.57438	–267.57106	–267.56956	–267.34412	–267.34701	–267.32156	–267.32146	–267.77219
•CH_2OCOCH_3	–267.59214	–267.59073	–267.60740	–267.60602	–267.58267	–267.70516	–267.57463	–267.57329	–267.56990	–267.56845	–267.34279	–267.34602	–267.32022	–267.32057	–267.76997
CH_3CN	–132.66766	–132.66766	–132.67728	–132.67728	–132.65512	–132.73478	–132.66583	–132.66583	–132.66167	–132.66167	–132.54593	–132.54752	–132.52665	–132.52665	–132.75467
•CH_2CN	–132.01898	–132.01540	–132.03087	–132.02671	–132.01212	–132.08632	–132.01910	–132.01827	–132.01522	–132.01379	–131.89323	–131.89430	–131.87587	–131.87525	–132.10263

CH_3NO_2	–244.91797	–244.91797	–244.93025	–244.93025	–244.92728	–245.01220	–244.91446	–244.91446	–244.90641	–244.90641	–244.70583	–244.70837	–244.69274	–244.69274	–245.09607
$•CH_2NO_2$	–244.26218	–244.26020	–244.27500	–244.27289	–244.27554	–244.35579	–244.26042	–244.25913	–244.25244	–244.25095	–244.04539	–244.04748	–244.03385	–244.03381	–244.43655
•H	–0.49862	–0.49862	–0.49782	–0.49782	–0.49766	–0.49921	–0.49861	–0.49861	–0.49818	–0.49818	–0.50171	–0.50179	–0.49982	–0.49982	–0.49999

[a] Including scaled (by 0.9806) RB3-LYP/6-31G(d) ZPVEs.

[b] Energy calculations carried out with the 6-311+G(3df,2p) basis set on RB3-LYP/6-31G(d) geometries.

[c] W1′ calculations for systems containing second- and third-row elements.

TABLE S2: Comparison of Calculated Bond Dissociation Energies for $CH_3X \rightarrow \bullet CH_2X + \bullet H$ with Experimental Values (0 K, kJ mol^{-1})

Radical($\bullet CH_2X$)	UBMK	RBMK	UMPWB1K	RMPWB1K	UM05	UM05-2X	UB2-PLYP	RB2-PLYP	UMPW2-PLYP	RMPW2-PLYP	G3(MP2)-RAD	G3X(MP2)-RAD	CBS-QB3	ROCBS-QB3	W1 [a]	Experiment [b]
$\bullet CH_3$	430.6	434.7	430.4	434.3	425.4	427.8	423.3	427.1	423.8	427.7	428.4	429.1	434.2	433.4	432.3	432.4 ± 0.4
$\bullet CH_2NH_2$	376.5	380.4	375.8	380.1	373.9	376.2	371.6	375.2	372.6	376.5	384.1	383.9	384.6	383.9	383.0	386.8 ± 8.4
$\bullet CH_2OH$	391.5	395.3	391.1	395.2	388.8	392.4	386.7	390.2	387.6	391.5	396.8	396.6	399.1	398.5	397.0	395.8 ± 0.63
$\bullet CH_2OCH_3$	391.3	394.9	393.0	395.5	388.8	392.9	386.4	389.8	387.5	391.3	397.3	397.1	399.4	398.9	397.1	395.7 [c]
$\bullet CH_2F$	414.3	417.9	412.8	416.6	410.6	414.2	407.7	411.3	408.6	412.4	415.9	416.0	419.6	419.0	417.5	417.4 ± 4.2
$\bullet CH_2CH_3$	413.1	417.6	411.3	415.5	402.9	410.3	405.9	409.9	406.6	410.7	414.2	414.5	418.0	417.3	416.5	413.0 ± 1.3
$\bullet CH_2CH_2CH_3$	416.2	420.5	415.3	419.1	406.4	413.6	409.1	412.9	409.8	413.9	415.9	417.8	420.9	420.1	419.6	414.8 ± 2.1
$\bullet CH_2CF_3$	436.5	440.8	435.8	438.7	425.8	433.4	427.4	431.2	428.4	432.4	436.1	434.8	440.8	440.0	438.4	439.3 ± 4.5
$\bullet CH_2CF_2CF_3$	433.0	437.3	433.1	435.5	422.8	430.5	424.5	428.3	425.5	429.5	433.3	433.2	437.3			
$\bullet CH_2PH_2$	399.7	404.5	399.5	404.7	391.7	399.6	394.6	399.0	395.3	400.1	405.1	405.2	405.8	405.9	405.4 [a]	
$\bullet CH_2SH$	392.7	397.4	387.0	392.1	381.6	387.3	382.5	386.5	383.5	388.0	392.2	391.8	392.8	392.5	390.9 [a]	386.3 ± 8.4
$\bullet CH_2Cl$	409.9	414.5	404.0	408.7	398.4	404.8	400.1	404.2	400.9	405.4	407.2	406.7	410.5	410.1	409.3 [a]	411.9 ± 2.3
$\bullet CH_2Br$	412.8	417.5	409.8	414.6	402.7	414.1	406.3	410.3	407.1	411.4			424.1			410.3 ±2.4
$\bullet CH_2BH_2$	382.8	385.9	386.0	388.6	381.8	385.0	380.5	383.2	381.1	383.9	388.3	388.2	391.5	391.8	391.4	
$\bullet CH_2CH{=}CH_2$	356.0	368.2	353.2	367.0	340.3	351.3	351.5	356.6	351.5	358.7	357.7	358.0	359.4	359.0	362.0	363.5 ± 3

•$CH_2C{\equiv}CH$	371.4	381.7	368.5	380.0	357.7	368.8	367.4	370.6	367.9	372.8	375.7	376.2	376.1	377.3	378.7	377.7 ± 4.2[d]
•$CH_2C_6H_5$	368.4	377.9	366.8	377.4	353.4	365.7	368.8	368.8	368.7	370.7	369.5	369.8	374.3	370.2	373.2	370.7 ± 5.0
•CH_2CHO	390.0	398.9	387.4	397.5	382.4	385.9	386.5	389.0	386.6	390.6	393.4	393.1	393.3	394.9	395.8	392.6[c, e]
•CH_2COOH	405.3	410.7	403.7	409.0	395.4	401.4	398.0	401.4	398.7	402.7	407.2	406.9	409.1	409.4	408.6	407.7 ± 3.3[f]
•CH_2COOCH_3	405.0	410.3	403.5	408.4	394.6	401.3	397.5	400.9	398.3	402.2	406.8	406.3	408.8	409.0	409.0	401.1 ± 10.5[g]
•CH_2OCOCH_3	405.3	409.0	405.0	408.6	398.8	406.7	400.2	403.7	401.3	405.1	410.3	408.9	412.3	411.4	414.8	398.4[c]
•CH_2CN	394.0	403.4	390.1	401.1	381.6	391.9	388.9	391.0	389.3	393.0	396.4	397.6	396.4	398.0	399.2	399.5 ± 4.2
•CH_2NO_2	412.6	417.8	413.3	418.9	404.6	412.8	408.1	411.5	409.0	412.9	416.8	417.7	417.7	417.8	418.8	409.7[c]
MD (W1)[h]	–4.5	1.1	–6.0	–0.1	–13.0	–6.4	–10.3	–6.9	–9.6	–5.5	–2.1	–2.0	0.3	0.0		
MAD (W1)[h]	4.8	3.0	6.0	1.8	13.0	6.4	10.3	6.9	9.6	5.5	2.3	2.2	1.7	1.3		
LD (W1)[h]	–9.6	6.5	–10.1	–6.2	–21.7	–10.8	–11.5	–11.1	–13.5	–9.7	–4.5	–5.9	–2.8	–3.5		
MD (Expt)[c, g, h]	–2.5	3.4	–4.8	1.5	–12.2	–4.9	–8.8	–5.3	–8.1	–3.9	–1.3	–1.2	2.4	0.8	0.7	
MAD (Expt)[c, g, h]	3.9	4.3	4.9	3.1	12.2	5.5	8.8	5.4	8.1	4.3	2.8	2.8	4.0	2.5	2.1	
LD (Expt)[c, g, h]	–10.2	11.1	–10.9	6.6	–23.2	–12.2	–15.1	–11.6	–14.1	–10.3	5.9	±5.5	13.8	6.2	4.8	

[a] W1' calculations for systems containing second- and third-row elements. [b] Bond dissociation energies at 0 K calculated using experimental BDEs at 298 K from ref 1, unless otherwise noted, with the thermal corrections to 0 K obtained at the RB3-LYP/6-31G(d) level. [c] Species without experimental error bars are not included in the statistics. [d] Calculated using the experimental BDE for propyne reported by Tsang.[2] [e] Calculated using the experimental BDE for acetaldehyde reported by Cummings and Kebarle.[3] [f] Calculated using the experimental

BDE for acetic acid reported by Lagoa et al.[4] [g] Species with experimental uncertainties greater than ± 10 kJ mol^{-1} are not included in the statistics. [h] MD, MAD and LD are mean deviation, mean absolute deviation and largest deviation, respectively, from W1 and experimental values.

TABLE S3: Comparison of Calculated Radical Stabilization Energies with Experimental Values (0 K, kJ mol^{-1})

Radical(•CH_2X)	UBMK	RBMK	UMPWB1K	RMPWB1K	UM05	UM05-2X	UB2-PLYP	RB2-PLYP	UMPW2-PLYP	RMPW2-PLYP	G3(MP2)-RAD	G3X(MP2)-RAD	CBS-QB3	ROCBS-QB3	W1[a]	Experiment[b]
•CH_2NH_2	54.1	54.4	54.5	54.3	51.5	51.6	51.6	51.9	51.1	51.2	44.2	45.2	49.5	49.5	49.3	45.6 ± 8.4
•CH_2OH	39.1	39.4	39.3	39.1	36.6	35.4	36.6	36.9	36.1	36.2	31.6	32.5	35.1	34.9	35.3	36.5 ± 0.63
•CH_2OCH_3	39.4	39.8	37.4	38.8	36.6	35.0	36.9	37.3	36.2	36.4	31.0	32.0	34.7	34.5	35.2	36.6[c]
•CH_2F	16.4	16.8	17.5	17.7	14.9	13.5	15.6	15.8	15.1	15.3	12.4	14.5	14.6	14.5	14.8	15.0 ± 4.2
•CH_2CH_3	17.5	17.1	19.1	18.8	22.5	17.5	17.4	17.2	17.2	17.0	14.1	14.5	16.2	16.2	15.8	19.3 ± 1.3
•$CH_2CH_2CH_3$	14.5	14.2	15.1	15.2	19.0	14.2	14.2	14.2	13.9	13.8	12.5	13.3	13.3	13.3	12.7	17.6 ± 2.1
•CH_2CF_3	–5.9	–6.1	–5.4	–4.4	–0.4	–5.6	–4.1	–4.1	–4.6	–4.7	–7.7	–5.7	–6.6	–6.6	–6.1	–6.9 ± 4.5
•$CH_2CF_2CF_3$	–2.4	–2.6	–2.8	–1.2	2.6	–2.6	–1.2	–1.2	–1.7	–1.7	–4.9		–3.1			
•CH_2PH_2	30.9	30.2	30.8	29.6	33.7	28.1	28.7	28.1	28.5	27.6	23.3	23.9	28.4	27.5	27.0	
•CH_2SH	37.9	37.4	43.4	42.2	44.0	40.5	40.8	40.5	40.3	39.7	36.1	37.3	41.4	40.9	41.4	46.1 ± 8.4
•CH_2Cl	20.7	20.2	26.4	25.6	27.1	22.9	23.2	22.9	22.8	22.4	21.1	22.4	23.7	23.3	23.0	20.5 ± 2.3
•CH_2Br	17.8	17.2	20.5	19.7	22.8	13.9	17.0	16.8	16.6	16.3			10.1			22.1 ±2.4
•CH_2BH_2	47.8	48.8	44.3	45.7	43.7	42.8	42.8	43.9	42.7	43.8	40.1	40.9	42.7	41.6	40.9	
•$CH_2CH{=}CH_2$	74.6	66.6	77.2	67.3	85.2	76.6	71.8	70.5	72.2	69.0	70.7	71.1	74.8	74.4	70.3	68.9 ± 3
•$CH_2C{\equiv}CH$	59.2	53.0	61.8	54.3	67.7	58.9	55.9	56.5	55.9	55.0	52.6	52.9	58.1	56.1	53.6	54.7 ± 4.2[d]
•$CH_2C_6H_5$	62.3	56.8	63.5	57.0	72.1	62.0	54.5	58.3	55.1	57.1	58.9	59.2	59.9	63.2	59.1	61.6 ± 5.0

•CH_2CHO	40.7	35.8	43.0	36.8	43.0	41.8	36.8	38.1	37.1	37.2	34.9	36.0	40.9	38.5	36.6	39.8[c,e]
•CH_2COOH	25.4	24.0	26.6	25.4	30.1	26.3	25.3	25.6	25.0	25.0	21.2	22.1	25.1	24.0	23.7	24.7 ± 3.3[f]
•CH_2COOCH_3	25.7	24.4	26.8	25.9	30.8	26.5	25.8	26.2	25.5	25.6	21.5	22.8	25.4	24.4	23.3	31.3 ± 10.5[g]
•CH_2OCOCH_3	25.4	25.7	25.4	25.7	26.6	21.1	23.1	23.4	22.5	22.6	18.0	20.2	21.9	22.0	17.5	34.0[c]
•CH_2CN	36.7	31.3	40.2	33.2	43.8	36.0	34.4	36.1	34.5	34.7	31.9	31.5	37.8	35.4	33.1	32.8 ± 4.2
•CH_2NO_2	18.0	16.9	17.0	15.4	20.9	15.0	15.2	15.6	14.7	14.8	11.6	11.4	16.5	15.6	13.5	22.7[c]
MD (W1)[h]	3.0	1.5	4.1	2.3	6.5	1.9	1.4	1.8	1.1	1.0	–2.0	–1.1	1.6	1.1		
MAD (W1)[h]	3.6	3.1	4.1	2.8	6.5	2.1	1.9	1.9	1.7	1.6	2.1	1.6	1.7	1.4		
LD (W1)[h]	–3.5	–4.0	8.2	8.2	14.9	6.3	5.6	5.9	–4.1	5.2	–5.3	–4.1	4.7	4.6		
MD (Expt)[c, g, h]	0.8	–1.1	3.0	0.5	5.6	0.4	–0.3	0.1	–0.5	–0.7	–2.8	–1.9	–0.4	0.2	–0.8	
MAD (Expt)[c, g, h]	3.3	3.2	4.0	2.7	5.9	3.5	3.0	2.8	2.9	2.6	3.2	2.8	3.6	2.6	2.1	
LD (Expt)[c, g, h]	–8.2	–8.7	8.9	8.7	16.3	–8.2	–7.1	6.3	–6.6	–5.8	–9.9	–8.8	–12.0	5.5	–4.9	

[a] W1' calculations for systems containing second- and third-row elements. [b] Bond dissociation energies at 0 K calculated using experimental BDEs at 298 K from ref 1, unless otherwise noted, with the thermal corrections to 0 K obtained at the RB3-LYP/6-31G(d) level. [c] Species without experimental error bars are not included in the statistics. [d] Calculated using the experimental BDE for propyne reported by Tsang.[2] [e] Calculated using the experimental BDE for acetaldehyde reported by Cummings and Kebarle.[3] [f] Calculated using the experimental BDE for acetic acid reported by Lagoa et al.[4] [g] For all species with experimental uncertainties less than ± 10 kJ mol^{-1}. [h] MD, MAD and LD are mean deviation, mean absolute deviation and largest deviation, respectively, from W1 and experimental values.

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