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New accurate reference energies for the G2/97 test set

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A recently proposed computational protocol is employed to obtain highly accurate atomization energies for the full G2/97 test set, which consists of 148 diverse molecules. This computational protocol is based on the explicitly correlated coupled-cluster method with iterative single and double excitations as well as perturbative triple excitations, using quadruple-ζ basis sets. Corrections for higher excitations and core/core-valence correlation effects are accounted for in separate calculations. In this manner, suitable reference values are obtained with a mean deviation of -0.75 kJ/mol and a standard deviation of 1.06 kJ/mol with respect to the active thermochemical tables. Often, in the literature, new approximate methods (e.g., in the area of density functional theory) are compared to, or fitted to, experimental heats of formation of the G2/97 test set. We propose to use our atomization energies for this purpose because they are more accurate on average. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4704796]

I. INTRODUCTION

The aim of the present paper is to provide highly accurate benchmark atomization energies for the G2/97 test set.[1,2] This is important because new quantum-chemical methods are often assessed with respect to, or fitted to, this test set. Until now, experimental heats of formation have been used as reference values. Their accuracy is sometimes questionable, however. For example, not only the heats of formation of certain molecules (e.g., COF_2) (Ref. 3) but also certain atomic reference values (e.g., Si) (Ref. 4) have been questioned. In particular, the use of uncertain reference values for *atomic* heats of formation has a large impact on the reference values for the molecules built from the respective atoms (such as Si). For example, the experimental heats of formation of the atoms Be and Al used for the heats of formation of the G2/97 test set also have unusually high experimental uncertainties (1 kcal/mol or more).[5] The high uncertainty of the experimental reference value for COF_2 has led Curtiss *et al.* to recommend to drop the molecule from the test set.[6] Other studies nevertheless compare their computed value to a doubtful reference value for the heat of formation of COF_2. Another problem lies in the fact that, usually, nonrelativistic methods are assessed with respect to, or fitted to, experimental reference values, which by nature contain relativistic effects. Furthermore, geometries and frequencies are often not easily accessible for new quantum-chemical methods. Therefore, B3LYP or MP2 structural parameters are usually used instead, which makes a comparison with experimental energies obscured by differences in geometry.

A much better assessment consists of comparing any set of new quantum-chemical results with the highly accurate benchmark atomization energies of the present study at fixed prescribed reference geometries, thereby avoiding all of the aforementioned problems. In such a direct assessment, one does not need to account for relativistic effects (including spin–orbit corrections), nor for Born–Oppenheimer diagonal corrections, nor for anharmonic zero-point vibrational energies, nor for finite-temperature effects.

Other studies with the aim to provide highly accurate theoretical reference data for atomization energies have also been reported for other test sets.[7–9] They contain subsets of the G2/97 test set, but no study with highly accurate computational reference data for the entire G2/97 test set has been reported yet. The G2/97 test set has been extended to the G3/99 (Ref 10) and the G3/05 test sets.[11] Many parameters of density functionals and composite schemes have been fitted to either the G2/97 or G3/99 test set. Subsets of the G2/97 test set have also been used to generate other training sets.[12] The AE6 test set[13] is a very small test set of six atomization energies, which are supposed to be representative for the Database/3 test set,[14] which consists of 109 atomization energies. Very recently, we provided highly accurate reference values for the AE6 test set.[15] The S22 test set[16] has been proposed for weak interactions, and the reference values were revised recently.[17,18] The mindless benchmark test set MB08-165[19] has been suggested to test approximate quantum-chemical methods in non-equilibrium geometries. The GMTKN30 test set[20] is a combination of 30 diverse subsets. It contains test sets for atomization energies, proton affinities, ionization potentials, electron affinities, barrier heights, reaction energies, and non-covalent interactions. Although the GMTKN30 test set is much more diverse than the G2/97 test set, the latter (which is much older than GMTKN30) test set has thus far been more popular for assessing new approximate quantum-chemical methods.

In the present work, we provide highly accurate theoretical atomization energies for all of the molecules in the G2/97 test set. This opens the possibility to assess or fit more approximate methods to our atomization energies. Very recently, we applied a new computational protocol based

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on explicitly correlated[21–29] coupled-cluster theory using iterative single and double excitations as well as perturbative triple excitations, CCSD(T)(F12),[27,30–36] to the popular AE6 and BH6 test sets.[15] In Ref. 15, we showed that our computed atomization energies are within chemical accuracy (the error estimates are below 1 kcal/mol). Furthermore, our calculated atomization energies agreed well with the even more accurate W4 method[37] from the Wn family of methods.[37–40] Besides being less expensive than W4 theory, a unique feature of our protocol is that it does not involve any extrapolation to the complete basis set limit. Rather, it relies on the CCSD(T)(F12) method to approach the basis set limit. The accuracy of this method[41–43] and other approximations to CCSD(T)-F12[44–46] have been demonstrated in many other works.

Very recently, Karton and Martin proposed the explicitly correlated Wn theories W1-F12 and W2-F12,[47] in which the coupled-cluster complete basis set limit is also approached using an F12 wave function expansion, as in the present work. They furthermore suggested to extrapolate to the complete basis set limit using the coupled-cluster F12 results.

In Sec. II, we provide a short description of the employed methods. Results are presented and discussed in Sec. III. In Sec. IV, a short summary and conclusions are presented.

II. METHODS

We employ the frozen-core CCSD(T)(F12) method augmented with higher-order corrections for core/core-valence correlation and higher-excitation effects. According to Ref. 42, an error of 0.1 kJ/mol is expected per valence electron using this computational protocol.[15] Errors of the core/core-valence correlation correction were found to be negligible in Ref. 15. We do not account for relativistic effects as most methods fitted or assessed using the G2/97 test set are non-relativistic methods. The employed geometries (B3LYP/6-31G(2df, p) level of theory) were taken from Ref. 48 and are provided as supplemental material.[49] All open-shell systems were treated using unrestricted methodologies.

A. Explicitly correlated calculations

The frozen-core CCSD(T)(F12) calculations were performed exactly as in Ref. 42. These calculations were done in the framework of ansatz 2, variant B, where the strong orthogonality projector

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \tag{1}$$

$$\hat{O}_\mu = \sum_i |\phi_i(\mu)\rangle \langle\phi_i(\mu)|, \qquad \hat{V}_\mu = \sum_a |\phi_a(\mu)\rangle \langle\phi_a(\mu)|,$$

with occupied orbitals ϕ_i and virtual orbitals ϕ_a,

is used, with sp cusp conditions[50] to predetermine the geminal amplitudes, and spin-flipped[25,50] geminals that are constructed from a linear combination of six Gaussian functions.[50,51] Note that ansatz 2 is much more efficient than ansatz 1 in recovering correlation energy. We provide the exponents and coefficients of the STG-6G approxima-

tion to the correlation factor in the supplemental material.[49] The CCSD(T)(F12) calculations were performed with the program package TURBOMOLE.[52] For the elements H, B–F, and Al–Cl, explicitly correlated calculations employed the cc-pVQZ-F12 orbital basis sets[53] with the aug-cc-pwCV5Z auxiliary basis sets[54,55] recommended for RI-MP2 and RI-CC2 calculations and CABS basis sets[56] recommended for RI-MP2-F12 and RI-CCSD(F12) calculations from the TURBOMOLE basis set library. In the TURBOMOLE implementation of CCSD(T)(F12) theory, the resolution of the identity (RI) approximation is used for some of the two-electron integrals. For the elements Li, Be, and Na, the cc-pCVQZ-F12 orbital basis sets,[57] auxiliary basis sets (cc-pV5Z),[54,55] and CABS basis sets[57] were used. The 1s electrons of the atoms B–Na were kept frozen, as well as the 1s, 2s, and 2p electrons of the atoms Al–Cl. The geminal exponent of 1.1 a_0^{-1} was used throughout. The perturbative CABS singles correction[58] (E_{CABS}) was taken into account.

B. Conventional calculations

Conventional all-electron and frozen-core CCSD(T)[59] calculations employing the cc-pwCVQZ basis sets[60] in conjunction with the RI basis sets[54,55] recommended for RI-MP2 and RI-CC2 calculations were used to estimate the core/core-valence correlation energies. In the TURBOMOLE implementation of CCSD(T) theory, the RI approximation is used for some of the two-electron integrals. Higher-excitation (difference between frozen-core CCSDT(Q)[61] and CCSD(T) calculations) contributions were calculated using the programs CFOUR[62] and MRCC.[63,64] The higher-excitation contributions were computed using the cc-pVDZ basis sets[65] in the case of H and Li–Na and the cc-pV(D+d)Z basis sets[66] for Al–Cl. The frozen-core definition is the same as for the CCSD(T)(F12) calculations, as described in Sec. II A. All TURBOMOLE calculations use the density convergence criterion of 10^{-10} a.u. while all CFOUR calculations use default convergence criteria.

C. Vibrational and relativistic corrections

We do not include vibrational and relativistic corrections in our reference values, but use the harmonic zero-point vibrational energy (ZPVE), anharmonic correction, and relativistic contributions from Ref. 43 to derive electronic energies from experimental reference values at 0 K. We denote the sum of these corrections as δ_{other}.

III. RESULTS AND DISCUSSION

A. Atomization energies for the G2/97 test set

Table I presents our frozen-core and all-electron correlated non-relativistic reference values for the atomization energies of the molecules in the G2/97 test set. The atomization energies reported under "$E_{ref. FC}$" are frozen-core values at the CCSD(T)(F12)/cc-pVQZ-F12 level of theory corrected for higher-excitation contributions ($E_{CCSDT(Q)/cc-pV(D+d)Z} - E_{CCSD(T)/cc-pV(D+d)Z}$). Core/core-valence correlation

TABLE I. Atomization energies of the G2/97 test set from the present work in kJ/mol.

Formula	Name	$E_{\text{ref. FC}}$[a]	$E_{\text{ref.non.-rel.}}$[b]
AlCl$_3$	Aluminum trichloride	1311.49	1310.70
AlF$_3$	Aluminum trifluoride	1808.29	1807.99
BCl$_3$	Boron trichloride	1352.15	1359.87
BF$_3$	Boron trifluoride	1963.98	1972.30
BeH	Beryllium monohydride	212.50	212.50
CCl$_4$	Tetrachloromethane	1312.24	1318.96
CF$_4$	Tetrafluoromethane	2000.29	2005.71
CH	Methylidyne radical	350.91	351.60
CH$_2$Cl$_2$	Dichloromethane	1548.52	1554.42
CH$_2$F$_2$	Difluoromethane	1827.75	1832.86
CH$_2$O$_2$	Formic acid	2093.28	2100.94
CH$_2$O	Formaldehyde	1561.51	1567.43
CH$_2$	Singlet carbene	755.71	757.45
CH$_2$	Triplet carbene	793.88	797.23
CH$_3$Cl	Chloromethane	1650.66	1656.17
CH$_3$	Methyl radical	1282.77	1287.21
CH$_3$O	Hydroxymethyl radical	1709.38	1715.47
CH$_3$O	Methoxy radical	1668.97	1674.66
CH$_3$S	Methylthio radical	1595.13	1601.03
CH$_4$	Methane	1752.56	1757.82
CH$_4$O	Methanol	2141.49	2147.84
CH$_4$S	Thiomethanol	1981.10	1987.63
CHCl$_3$	Trichloromethane	1438.15	1444.48
CHF$_3$	Trifluoromethane	1919.52	1924.71
CHO	Formyl radical	1164.33	1169.59
CN	Cyano radical	753.39	758.56
CNH	Hydrogen cyanide	1303.41	1310.97
CNH$_3$O$_2$	Methyl nitrite	2499.90	2507.94
CNH$_3$O$_2$	Nitromethane	2508.86	2518.40
CNH$_5$	Methylamine	2427.06	2434.89
C$_2$Cl$_4$	Tetrachloroethylene	1963.63	1976.57
C$_2$F$_4$	Tetrafluoroethylene	2458.80	2470.91
C$_2$H	Ethynyl radical	1103.15	1112.08
C$_2$H$_2$	Acetylene	1685.16	1695.79
C$_2$H$_2$O$_2$	Glyoxal	2645.79	2657.71
C$_2$H$_2$O	Ketene	2220.04	2232.05
C$_2$H$_3$Cl	Vinyl chloride	2265.70	2276.50
C$_2$H$_3$	Vinyl radical	1855.58	1864.92
C$_2$H$_3$F	Vinyl fluoride	2389.99	2400.61
C$_2$H$_3$O	Carbonyl methane	2426.20	2436.67
C$_2$H$_3$OCl	Acetyl chloride	2787.13	2798.87
C$_2$H$_3$OF	Acetyl fluoride	2946.26	2957.91
C$_2$H$_4$	Ethylene	2348.65	2358.75
C$_2$H$_4$O$_2$	Acetic acid	3350.83	3363.76
C$_2$H$_4$O$_2$	Methyl formate	3280.39	3292.61
C$_2$H$_4$O	Acetaldehyde	2824.22	2835.43
C$_2$H$_4$O	Oxirane	2714.69	2725.51
C$_2$H$_4$S	Thiirane	2609.09	2620.57
C$_2$H$_5$Cl	Ethyl chloride	2887.09	2897.60
C$_2$H$_5$	Ethyl radical	2516.37	2526.01
C$_2$H$_5$O	Ethoxy radical	2908.38	2919.13
C$_2$H$_6$	Ethane	2971.49	2981.64
C$_2$H$_6$O	Dimethyl ether	3330.63	3341.56
C$_2$H$_6$O	Ethanol	3381.59	3392.98
C$_2$H$_6$OS	Dimethyl sulfoxide	3574.86	3587.65
C$_2$H$_6$S	Dimethyl sulfide	3206.19	3217.58
C$_2$H$_6$S	Thioethanol	3210.77	3222.30
C$_2$N$_2$	Cyanogen	2084.80	2100.20
C$_2$NF$_3$	Trifluoroacetonitril	2675.64	2688.27

TABLE I. (*Continued.*)

Formula	Name	$E_{\text{ref. FC}}$[a]	$E_{\text{ref.non.-rel.}}$[b]
C$_2$NH$_3$	Acetonitrile	2565.94	2578.87
C$_2$NH$_5$	Aziridine	3000.47	3012.94
C$_2$NH$_5$O	Acetamide	3618.80	3633.73
C$_2$NH$_7$	Dimethylamine	3627.84	3640.55
C$_2$NH$_7$	Ethylamine	3662.09	3674.87
C$_3$H$_4$	Allene	2928.72	2944.45
C$_3$H$_4$	Cyclopropene	2836.78	2852.25
C$_3$H$_4$	Propyne	2934.48	2950.50
C$_3$H$_6$	Cyclopropane	3555.66	3571.30
C$_3$H$_6$O	Acetone	4080.98	4097.39
C$_3$H$_6$	Propene	3587.40	3602.67
C$_3$H$_7$Cl	1-Chloropropane	4115.27	4130.72
C$_3$H$_7$	Isopropyl radical	3755.06	3769.88
C$_3$H$_8$O	Methoxyethane	4571.15	4587.12
C$_3$H$_8$O	Isopropyl alcohol	4624.64	4641.05
C$_3$H$_8$	Propane	4199.18	4214.27
C$_3$NH$_3$	Acrylonitrile	3173.61	3191.46
C$_3$NH$_9$	Trimethylamine	4840.35	4857.95
C$_4$H$_{10}$	Isobutane	5433.13	5453.18
C$_4$H$_{10}$	*n*-Butane	5427.17	5447.22
C$_4$H$_4$O	Furan	4142.37	4164.49
C$_4$H$_4$S	Thiophene	4016.15	4038.49
C$_4$H$_6$	1,3-Butadiene	4217.43	4237.73
C$_4$H$_6$	2-Butyne	4179.82	4201.18
C$_4$H$_6$	Bicyclo[1.1.0]butane	4105.06	4125.62
C$_4$H$_6$	Cyclobutene	4170.00	4189.71
C$_4$H$_6$	Methylenecyclopropane	4133.88	4154.81
C$_4$H$_8$	Cyclobutane	4791.64	4811.19
C$_4$H$_8$	Isobutene	4829.32	4849.73
C$_4$H$_9$	*tert*-Butyl radical	4996.68	5016.63
C$_4$NH$_5$	Pyrrole	4464.55	4488.94
C$_5$H$_8$	Spiropentane	5350.47	5376.77
C$_5$NH$_5$	Pyridine	5155.83	5183.94
C$_6$H$_6$	Benzene	5696.88	5727.81
Cl$_2$	Dichlorine	247.16	248.22
CO	Carbon monoxide	1083.14	1087.57
CO$_2$	Carbon dioxide	1625.87	1633.95
COF$_2$	Carbonyl fluoride	1755.19	1762.10
COS	Carbonyl sulfide	1398.66	1406.74
CS	Carbon monosulfide	715.40	719.47
CS$_2$	Carbon disulfide	1165.93	1174.07
FCl	Chlorine monofluoride	261.80	262.43
F$_2$	Difluorine	162.15	162.31
F$_3$Cl	Chlorine trifluoride	537.00	537.44
HCl	Hydrogen chloride	448.52	449.58
HF	Hydrogen fluoride	592.09	593.02
HOCl	Hypochlorous acid	693.67	695.38
HO	Hydroxyl radical	447.50	448.30
HS	Mercapto radical	365.64	366.55
H$_2$	Dihydrogen	457.73	457.73
H$_2$O$_2$	Hydrogen peroxide	1124.05	1126.34
H$_2$O	Water	973.05	974.94
H$_2$S	Hydrogen sulfide	766.92	768.72
LiF	Lithium fluoride	583.12	583.99
LiH	Lithium hydride	242.27	242.27
Li$_2$	Dilithium	101.24	101.24
Na$_2$	Disodium	71.55	71.78
NaCl	Sodium chloride	411.98	412.96
NF$_3$	Trifluoroamine	862.79	863.68
NH$_2$	Amino radical	761.30	762.95

TABLE I. (*Continued.*)

Formula	Name	$E_{\text{ref. FC}}$[a]	$E_{\text{ref.non.−rel.}}$[b]
NH_3	Ammonia	1242.94	1245.99
NH	Imidogen	346.38	347.02
NO_2	Nitrogen dioxide	950.01	954.10
$NOCl$	Nitrosyl chloride	801.10	803.43
NO	Nitric oxide	636.75	639.28
N_2	Dinitrogen	951.59	955.82
N_2H_4	Hydrazine	1827.15	1832.69
N_2O	Nitrous oxide	1127.48	1133.70
OCl	Monochlorine monoxide	270.00	271.20
OF_2	Difluorine monoxide	392.34	392.68
OS	Sulfur monoxide	526.33	528.72
O_2	Dioxygen	504.36	505.88
O_2S	Sulfur dioxide	1086.86	1091.61
O_3	Ozone	614.29	615.78
P_2	Diphosphorus	485.14	489.29
PF_3	Phosphorus trifluoride	1527.81	1530.92
PH_2	Phosphino radical	644.21	645.47
PH_3	Phosphane	1010.33	1012.24
S_2	Disulfur	431.42	433.94
$SiCH_6$	Methylsilane	2626.11	2631.54
$SiCl_4$	Silicon tetrachloride	1625.41	1627.56
SiF_4	Silicon tetrafluoride	2416.45	2419.74
SiH_2	Singlet silylene	642.99	643.11
SiH_2	Triplet silylene	557.56	555.72
SiH_3	Silyl radical	954.30	953.44
SiH_4	Silane	1358.08	1357.91
SiO	Silicon monoxide	804.83	809.19
Si_2H_6	Disilane	2240.41	2240.54
Si_2	Disilicon	307.15	307.75

[a]Frozen-core non-relativistic atomization energy from the present work.
[b]Non-relativistic atomization energy from the present work.

corrections $(E_{\text{AE−CCSD(T)/cc−pwCVQZ}} - E_{\text{FC−CCSD(T)/cc−pwCVQZ}})$ were added to obtain the atomization energies reported under "$E_{\text{ref.non.−rel.}}$." The 148 molecules of the G2/97 test set contain closed-shell molecules as well as open-shell radicals composed of the elements H, Li-F, Na, and Al-Cl. Among them are 69 hydrocarbons (47 of them substituted), 15 inorganic hydrids, 35 non-hydrogen molecules, and 29 radicals.

Let us now compare the atomization energy of one of the larger molecules of the G2/97 test set, benzene, with previously published values. Martin and de Oliveira[38] proposed a value of 5730.7 kJ/mol, Feller and Dixon[67] published an atomization energy of 5725.4 kJ/mol, Parthiban and Martin[68] calculated 5732.8 kJ/mol, Karton *et al.*[69] proposed a value of 5730.1 kJ/mol, and most recently, Harding *et al.*[70] calculated 5728.9 kJ/mol. Note that the studies in Refs. 38 and 67–70 calculated more contributions (ZPVE, relativistic contributions, etc.) than we do, as the scope of our study is different. We do not aim to compare to experimental values. Fortunately, the prior studies also provide plain electronic energies, which makes a comparison to our numbers easy. The atomization energies proposed by Harding *et al.* and Karton *et al.* are probably more accurate than those of the other works because their studies include higher level corrections than those from Martin *et al.*, Feller and Dixon, and Parthiban and Martin. Our

atomization energy for benzene is 5727.8 kJ/mol. This value is very close to the most recent value derived by Harding and co-workers.

B. Error estimation

From our very recent study[15] and previous assessments of explicitly correlated coupled-cluster theory,[42] one would expect an error of 0.1 kJ/mol per valence electron for atomization energies. Table II presents a comparison of 26 of our atomization energies with data from the active thermochemical tables (ATcT data) (Ref. 43) and with the W4 values.[9] These 26 molecules represent the intersection of the ATcT values from Ref. 43, the W4 values from Ref. 9, and the G2/97 test set. Indeed, 23 of the compared molecules show a deviation from ATcT and W4 within or below the expected error of 0.1 kJ/mol per valence electron. The three cases with a larger deviation deserve a more detailed discussion. For singlet CH_2, we would expect an error up to about 0.6 kJ/mol. However, we find a deviation of -1.7 kJ/mol (-1.4 kJ/mol) with respect to W4 (ATcT). The ATcT value is between the W4 value and our atomization energy. At least partly, the deviation is due to the B3LYP geometry. The CCSD(T)(F12) energy using a structure optimized at the CCSD(T)/cc-pVQZ level of theory is 0.47 kJ/mol lower than for the structure we used. The source for the remaining difference might be that multi-reference effects in singlet CH_2 are not sufficiently captured by our higher-excitation correction, which at most involves CCSDT(Q). It does not seem to be related to the ZPVE. The ΔATcT$-\delta_{\text{other}}$ value of Table II for singlet CH_2 contains the anharmonic ZPVE of 43.15 kJ/mol taken from Ref. 43. A much more accurate value is 44.27 kJ/mol,[72] and taking this value would yield a ΔATcT$-\delta_{\text{other}}$ value of 760.0 kJ/mol, even further away from our value (757.5 kJ/mol).

The other two molecules for which we found larger-than-expected deviations from ATcT and W4 are ammonia and H_2. In both cases, the W4 value is between our atomization energy and the ATcT value. For ammonia, the deviation with respect to the ATcT value is twice as large as expected. As the deviation between our and the W4 value is rather small, the deviation with respect to the ATcT value is probably due to effects not accounted for in our computational protocol. The ΔATcT$-\delta_{\text{other}}$ value for ammonia contains the anharmonic ZPVE of 89.47 kJ/mol taken from Ref. 43. A much more accurate value is 88.87 kJ/mol,[71] and hence, an improved ΔATcT$-\delta_{\text{other}}$ value would be equal to 1247.2 kJ/mol, in much better agreement with our value (within 1.2 kJ/mol). This observation, however, strongly supports our viewpoint of using highly accurate computational reference values in place of experimental values. It is the purpose of purely computational reference values to *avoid* discussions about geometries, ZPVEs, and the like.

For H_2, the reason for the deviation of our value can only be the basis set incompleteness of either the Hartree-Fock or CCSD energy, but we note that this molecule is rather special because it has only two valence electrons. In summary, it is gratifying to observe that our computed atomization energies agree well with the ATcT values as well as with those from W4 theory, within the expected accuracy.

TABLE II. Comparison of 26 selected atomization energies from the G2/97 test set with W4 theory and ATcT values in kJ/mol.

| Formula	Name	$E_{\text{ref.non.}-\text{rel.}}$	E_{W4}[a]	ATcT$-\delta_{\text{other}}$[b]	ΔW4[c]	ΔATcT$-\delta_{\text{other}}$[d]
CF_4	Tetrafluoromethane	2005.7	2003.1	2004.7	2.6	1.0
CH_2	Singlet carbene	757.5	759.2	758.9	−1.7	−1.4
CH_2F_2	Difluoromethane	1832.9	1831.2	1834.0	1.7	−1.1
CH_2O_2	Formic acid	2100.9	2100.0	2101.4	0.9	−0.5
CH_4O	Methanol	2147.8	2148.5	2149.7	−0.7	−1.9
CO	Carbon monoxide	1087.6	1086.7	1087.0	0.9	0.6
COF_2	Carbonyl fluoride	1762.1	1759.9	1763.2	2.2	−1.1
CO_2	Carbon dioxide	1634.0	1632.4	1632.8	1.6	1.2
C_2H_2	Acetylene	1695.8	1696.7	1696.6	−0.9	−0.8
$C_2H_2O_2$	Glyoxal	2657.7	2657.3	2656.7	0.4	1.0
C_2H_4	Ethylene	2358.8	2360.2	2359.6	−1.4	−0.8
C_2H_4O	Oxirane	2725.5	2726.0	2727.3	−0.5	−1.7
C_2H_6O	Ethanol	3393.0	3394.2	3395.1	−1.2	−2.1
C_3H_4	Propyne	2950.5	2952.3	2952.6	−1.8	−2.1
C_3H_6	Propene	3602.7	3604.8	3604.5	−2.1	−1.8
C_3H_8	Propane	4214.3	4217.1	4216.2	−2.8	−1.9
F_2	Difluorine	162.3	163.4	163.5	−1.1	−1.2
HF	Hydrogen fluoride	593.0	592.6	593.1	0.4	−0.1
H_2	Dihydrogen	457.7	458.1	458.2	−0.4	−0.5
H_2CO	Formaldehyde	1567.4	1567.6	1567.7	−0.2	−0.3
H_2O	Water	974.9	974.8	975.4	0.1	−0.5
H_2O_2	Hydrogen peroxide	1126.3	1125.9	1127.2	0.4	−0.9
NH_3	Ammonia	1246.0	1246.9	1247.8	−0.9	−1.8
N_2	Dinitrogen	955.8	956.0	955.7	−0.2	0.1
OF_2	Difluorine monoxide	392.7	392.4	391.7	0.3	1.0
O_3	Ozone	615.8	616.8	617.7	−1.0	−1.9

[a]W4 values were taken from Ref. 9.
[b]ATcT values were taken from Ref. 43. δ_{other} are corrections for zero-point energy, anharmonicity, and relativistic effects from Ref. 43.
[c]ΔW4 denotes the deviation of $E_{\text{ref.non.}-\text{rel.}}$ with respect to W4 values.
[d]Δ ATcT$-\delta_{\text{other}}$ denotes the deviation of $E_{\text{ref.non.}-\text{rel.}}$ with respect to ATcT$-\delta_{\text{other}}$ values.
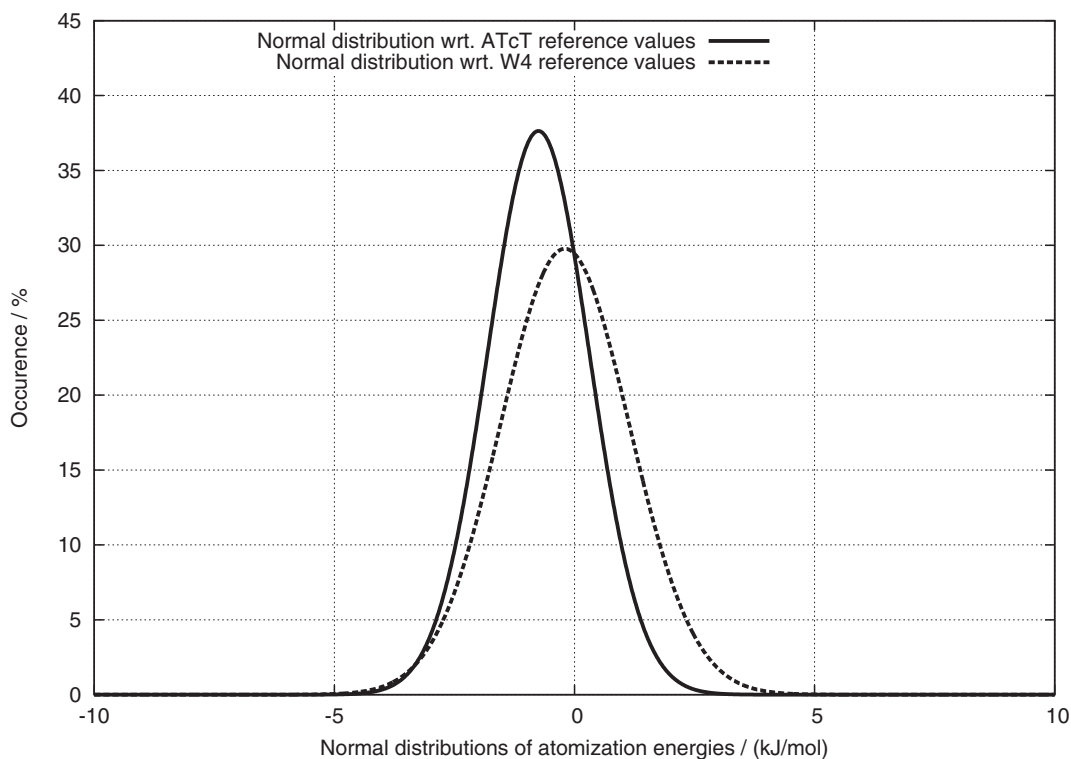
FIG. 1. Normal distributions in % of deviations of our atomization energies with respect to ATcT values (solid curve) and W4 theory (dashed curve) in kJ/mol.

TABLE III. Mean absolute deviations (MAD), mean deviations (MD), standard deviations σ (SD), and root mean square deviations (RMSD) for 26 atomization energies with respect to W4 theory and ATcT values in kJ/mol.

	w.r.t. W4	w.r.t. ATcT
MAD	1.10	1.13
MD	-0.20	-0.75
SD	1.34	1.06
RMSD	1.33	1.28

C. Statistical analysis

The normal distributions of the deviations of our atomization energies with respect to the ATcT values as well as with respect to those obtained using W4 theory are shown in Fig. 1. Table III presents mean absolute deviations, mean deviations, standard deviations σ, and root mean square deviations for 26 atomization energies with respect to W4 theory and ATcT values in kJ/mol. The presented statistical data show that our atomization energies are on average closer to W4 theory than to ATcT. With a standard deviation σ of 1.06 kJ/mol (1.34 kJ/mol) and mean error of -0.75 kJ/mol (-0.20 kJ/mol) with respect to ATcT (W4), we expect that the calculated atomization energies for 95% of the molecules have errors within the range $+1.33/-2.83$ kJ/mol ($+2.43/-2.83$ kJ/mol). Although our atomization energies are closer to the W4 values than to the ATcT values, we observe a larger spread with respect to W4 theory. This might be due to the fact that the ATcT values are slightly more accurate than the W4 data. As both computed values (ours and those from W4 theory) have a certain error spread, the larger standard deviation with respect to W4 data is explicable.

IV. CONCLUSIONS

In summary, we have presented highly accurate atomization energies for all 148 molecules of the test set G2/97. For a subset of 26 molecules, we calculated atomization energies with a standard deviation of 1.06 kJ/mol (1.34 kJ/mol) with respect to ATcT (W4) data. This opens the possibility to assess or fit new, approximate computational approaches to the benchmark atomization energies of the G2/97 test set. According to the standard deviation of our atomization energies with respect to the corresponding ATcT values, 95% of the atomization energies are within 2.1 kJ/mol and 99.9% of the atomization energies are within 3.5 kJ/mol (both within the chemical accuracy of 1 kcal/mol) of our calculated values. Thus, we expect our G2/97 atomization energies to be more accurate on average and more useful than the G2/97 heats of formation that have been used until now.

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