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Systematic Errors in ab Initio Bond Dissociation Energies

Karl K. Irikura*

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Bond dissociation energies (D_0) for 41 small molecules were calculated at 19 levels of ab initio theory up to CCSD(T)/cc-pVTZ, using geometries and vibrational zero-point energies from B3LYP/6-31G* hybrid density-functional calculations. Empirical correlations between the errors in the ab initio bond strengths and the following quantities were examined: (1) the distance between the bonded atoms, (2) the electron density at the midbond critical point, and (3) the contribution of dynamic electron correlation to the bond strength. Correlation 1 is related to the BAC-MP4 method of Melius and co-workers, and correlation 3 corresponds to the SAC methods of Truhlar, Gordon, and co-workers and to the PCI methods of Siegbahn, Blomberg, and co-workers. For each type of empirical correction, empirical estimates of the standard uncertainty for an arbitrary prediction are also provided. Type 3 correlations fail for bonds involving second-row elements (e.g., silicon), suggesting that the cc-pVTZ basis sets are not correlation balanced across the different periods. For the lighter elements, however, all three corrections are effective and could be refined into prescriptive methods.

Introduction

Driven by rapid progress in theory, applied mathematics, and computer speed, quantum chemistry is becoming increasingly useful throughout the subdisciplines of chemistry. One important application of theory is the prediction of reaction energetics. It is generally agreed that empirical corrections are needed to obtain quantitative molecular energetics from quantum chemical calculations.[1,2] Many approaches have been developed, often based upon chemically motivated functional forms for the empirical corrections. One of the oldest and most successful is the BAC-MP4 method (bond-additive corrections to energetics from fourth-order perturbation theory) developed by Melius and co-workers.[3−5] The corrections are based upon the bond lengths within the molecule of interest, with smaller corrections for nearest neighbors. This effects a parametrization of isodesmic reaction schemes.[6] At the time it was developed, BAC-MP4 was an expensive method employing the best theoretical methods [MP4/6-31G(d,p)]. It is now considered inexpensive and somewhat approximate but remains one of the most robust quantum-based approaches to molecular thermochemistry.[7,8] Perhaps the primary weakness of the BAC-MP4 method is its requirement for a substantial body of reliable thermochemical data to define many empirical parameters. However, as shown below, the number of parameters may be reduced dramatically by choosing a base calculation better than MP4/6-31G(d,p).

Another successful correction is based upon the observation that ab initio calculations that include electron correlation recover a constant fraction of the contribution of dynamic electron correlation to the bond strengths. This has been systematized in the "scaling-all-correlation" (SAC) methods of Truhlar, Gordon and co-workers[9−12] and the "parametrized configuration-interaction" (PCI) methods of Siegbahn, Blomberg, and co-workers.[13−16]

These concepts are investigated here at somewhat higher levels of theory (i.e., more complete treatment of electron correlation and larger basis sets) than done previously. Two relatively new tools are particularly relevant. (1) *Coupled-cluster techniques*,[17] such as CCSD(T),[18] include certain excitations to infinite order and are generally more accurate than finite-order perturbation methods such as MP4.[19] They are also more robust, being far more tolerant of spin contamination[20] and near-degeneracies.[21] (2) *Density-functional theory* (DFT) has been adopted by chemists and implemented in many quantum-chemistry software packages. DFT is based upon the fact that all the information about a (ground-state) system is contained in its electron density.[22] Like coupled-cluster methods, DFT methods are relatively insensitive to spin contamination[23] and to multireference character.[24] DFT is also popular because it is less expensive computationally than are conventional correlated methods.

In addition to the BAC-MP4 and SAC/PCI types of empirical scaling, another is tested here. Guided by the DFT concept and by the fact that the mean distance between electrons depends on their density, one might expect that empirical corrections could be based upon electron densities in chemical bonds. One might hope further that empirical parameters based upon electron density will not depend on the particular chemical elements that are joined by each bond.

The methods described above for deriving thermochemistry from ab initio calculations involve corrections that are intended to absorb all the shortcomings in the underlying theory. Popular alternatives, such as the G2 and the CBS families of methods, seek to estimate the results of very high-level calculations and minimize the role of empirical corrections.[25−31] In particular, Feller and Peterson recently extrapolated the performance of several ab initio theories to the basis set limit.[32] Although such thorough computations are not practical for routine use, they indicate the inherent reliability of the formal theories. Composite approaches such as G2 and CBS were not evaluated in

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[*] To whom correspondence should be addressed. E-mail karl.irikura@nist.gov.

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TABLE 1: Experimental Reference Data (Ideal Gas)[a]

molecule	$\Delta_f H^\circ_0$ (kJ/mol)	ref	molecule	$\Delta_f H^\circ_0$ (kJ/mol)	ref
H	216.035(6)	74	OH	34.4(12)	74
C	711.19(46)	74	H_2O	−238.921(42)	74
C(^{5}S)	1114.75(46)	74, 50	CO	−113.81(17)	74
N	470.82(10)	74	CO_2	−393.15(5)	74
O	246.79(10)	74	N_2	0	74
F	77.28(30)	74	NH_3	−38.9(4)	74
Si	446(8)	74	HCN	135.5(84)	74
Si(^{5}S)	845(8)	74, 75	NO	89.78(17)	74
P	315.6(10)	74	NO_2	35.93(80)	74
S	274.73(25)	74	F_2	0	74
Cl	119.621(6)	74	HF	−272.5(8)	74
H_2	0	74	CF_4	−927.2(13)	74
CH	593.5(21)	53	Cl_2	0	74
CH($^4\Sigma^-$)	665.1(21)	53, 51	HCl	−92.13(21)	74
CH_2	390.9(21)	53	CCl_4	−93.8(21)	74
CH_3	150.6(21)	53	H_2S	−17.6(8)	74
CH_4	−66.91(34)	74	SO_2	−294.30(21)	74
C_2	829.3(38)	74	SF_6	−1207.7(3)	76, 74
C_2H_2	227.3(8)	77, 74	PH_3	30.8(17)	74
C_2H_4	60.99(29)	74	PO	−27.5(32)	78
C_2H_6	−68.2(3)	79, 80	P_2	145.5(21)	74
C_3H_4 (allene)	198.0(11)	80, 79	P_4	66.2(21)	74
C_3H_5 (allyl)	184.5(21)	81	SiH_3	205.9(25)	53, 82
cy-C_3H_6	70.4(5)	79, 80	SiH_4	43.9(21)	74
C_6H_6 (benzene)	100.1(29)	80, 79	SiO	−101.6(84)	74
O_2	0	74	Si_2H_6	109(4)	83
O_3	145.3(17)	74			

[a] Reported uncertainties in the least significant digits are given in parentheses and are assumed to represent the standard uncertainty (1σ).

the present study, although some comparisons are made with the G2 method[33] because of its widespread use.

Technical Details

The molecules included in this survey, which are intended to be representative of common main-group compounds, are listed in Table 1 along with their reference enthalpies of formation at zero temperature. The reference data were not thoroughly evaluated but are believed to be sufficiently reliable to reveal any useful correlations between errors in D_0 (homolytic bond dissociation energy, including zero-point vibrational energy, at zero temperature) and parameters such as bond length (r_e), electron density at the bond critical point (ρ_b), or total contribution of electron correlation to D_0. Atomization and bond dissociation reactions are not isogyric[34] and are challenging for ab initio theory. Thus, they constitute a difficult test that is likely to reveal systematic errors in the calculated energetics.

ACES II[35,36] was used for the larger coupled-cluster calculations, and Gaussian94[37] was used for the rest of the calculations.[38] All open-shell calculations were spin-unrestricted. Molecular geometries were fully optimized using the B3LYP hybrid DFT method[39,40] and 6-31G(d) basis sets. The default integration grid was used for all DFT calculations. Harmonic vibrational frequencies were calculated at this same B3LYP/6-31G(d) level and scaled by the empirical factor of 0.9806 to obtain vibrational zero-point energies (ZPEs).[41] Electron densities were calculated at these geometries using the BLYP gradient-corrected density functional and 6-311+G(d,p) basis sets. The electron density was analyzed using the “atoms-in-molecules” (AIM) approach developed by Bader and co-workers,[42] as implemented[43] in the Gaussian94 program package.[37,38] BLYP was used instead of B3LYP because the HF contribution to the density in B3LYP is expected to be less physically reasonable than a “pure” DFT density.[22,44] Some other properties of the electron density at the bond critical point were investigated (e.g., eigenvalues of the Hessian) but were not found to provide correlations as strong as for the density itself.

Bond dissociation energies (D_0) or average bond dissociation energies ($\bar{D}_0$) were calculated at the HF, B3LYP, MP2, MP4(SDQ), MP4(SDTQ), CCD, CCSD, and CCSD(T) levels using 6-31G(d,p) and cc-pVTZ[45,46] basis sets. The latter basis sets are reasonably large: (5s,2p,1d)/[3s,2p,1d] on hydrogen, (10s,5p,2d,1f)/[4s,3p,2d,1f] on first-row elements, and (15s,9p,2d,1f)/[5s,4p,2d,1f] on second-row elements. Calculations were also done at the B3LYP/6-31G(d), B3LYP/6-311+G(d,p), and MP2/6-31G(d) levels. Core electrons were frozen in the correlated calculations (except for DFT). Among these methods, CCSD(T) is the most thorough and is expected to provide the best results. The 6-31G(d) basis set was not used for energy calculations because its lack of hydrogen polarization functions leads to poor correlation balance.[10]

Wherever reasonable, the high-spin dissociated limit was used for calculating bond energies. This procedure is intended to isolate most of the correlation error in the bonded, molecular calculation and not to reflect spin recoupling in the fragments. For example, the C≡C bond energy in acetylene is calculated as the ZPE-adjusted energy difference between two quartet methyne fragments (CH $^4\Sigma^-$) and the singlet molecule (HC≡CH).[47−49] Experimental excitation energies are used subsequently to derive thermodynamic bond strengths.[50,51]

For the SAC/PCI type of correction, the total contribution of electron correlation to the bond energy is approximated as the difference between the experimental bond energy (D_0 or, when several equivalent bonds are involved, $\bar{D}_0$) and the bond energy calculated at the uncorrelated Hartree−Fock (HF) level. The fraction of the electron correlation that is recovered, F, is then defined by eq 1.

$$F = \frac{D_{\text{correlated}} - D_{\text{HF}}}{D_{\text{expt}} - D_{\text{HF}}} = 1 - \frac{\text{error}_{\text{correlated}}}{\text{error}_{\text{HF}}} \qquad (1)$$

Results

The target experimental quantities are the average bond dissociation energies at 0 K. Experimental values are included in Table 2 for the bond strengths considered here. High-spin dissociated limits are used wherever reasonable. For example, the value of $\bar{D}_0$ for benzene is one-sixth the energy required to separate C_6H_6 into six CH($^4\Sigma^-$) fragments, after correcting by the experimental value of T_0 (CH $^4\Sigma^-$),[51] and the value for allene is one-half the energy required to separate C_3H_4 into two CH_2($^3B_1$) fragments and one C atom (^{5}S) fragment, after correcting by the experimental (*J*-averaged) excitation energy of quintet carbon atom.[50] Triplet O_2, however, is dissociated to triplet O atoms because the lowest quintet state of O is a highly excited Rydberg state expected to play little role in bonding. Spin−orbit corrections[52] are not included in the present survey study; the largest such corrections among the molecules considered here would be −7.0 kJ/mol for D_0 of Cl_2, −3.2 kJ/mol for F_2, and −2.7 kJ/mol for SiO. Bond strengths calculated at the HF/ and CCSD(T)/cc-pVTZ levels and changes in ZPE are also included in Table 2. The calculated bond lengths and electron densities (ρ_b) at the bond critical points are also listed in Table 2. Errors (viz., calculated minus experimental) at the CCSD(T)/cc-pVTZ level for bonds involving first-row elements or hydrogen are plotted in Figure 1 against the bond length r_e, as calculated at the B3LYP/6-31G(d) level. As usual, all the errors are negative. This systematic underbinding has been cleverly exploited to bracket the enthalpies of formation of simple carbon

TABLE 2: Bond Strengths (Including ZPE), Zero-Point Energies (ZPE), Bond Lengths, and Electron Densities

	D_0 or $\bar{D}_0$ (kJ/mol)					
reaction	expt[c]	HF[d]	CCSD(T)[d]	ΔZPE[a] (kJ/mol)	r_e (Å)[a]	ρ_b (au)[b]
$H_2 = 2H$	432.1	323.9	427.4	−26.1	0.743	0.262
$HF = H + F$	565.8(9)	374.7	548.7	−23.3	0.934	0.358
$H_2O = 2H + O$	458.9(1)	294.0	443.3	−54.4	0.969	0.360
$OH = O + H$	424.4(12)	259.7	408.8	−21.4	0.983	0.352
$NH_3 = N + 3H$	385.9(1)	247.9	372.1	−88.9	1.020	0.331
$CH_2(^3B_1) = C(^5S) + 2H$	578.0(11)	425.6	565.1	−44.8	1.082	0.275
$CH_3 = C(^5S) + 3H$	537.4(7)	395.5	526.5	−76.8	1.083	0.277
$CH_4 = C(^5S) + 4H$	511.5(1)	376.0	501.3	−116.4	1.094	0.269
$N_2 = 2N$	941.6(2)	459.2	890.1	−14.4	1.106	0.664
$CH = C + H$	333.7(21)	219.0	324.2	−16.4	1.133	0.264
$CO = C + O$	1071.8(5)	710.8	1039.5	−13.0	1.138	0.476
$HCN = CH(^4\Sigma^-) + N$	1000.4(87)	547.5	960.8	−24.2	1.157	0.476
$NO = N + O$	627.8(2)	206.2	587.2	−11.7	1.159	0.571
$CO_2 = C(^5S) + 2O$	1000.7(3)	621.3	967.8	−29.8	1.169	0.447
$NO_2 = N + 2O$	464.2(4)	97.5	431.8	−22.7	1.203	0.510
$C_2H_2 = 2CH(^4\Sigma^-)$	1102.9(43)	679.8	1062.6	−32.3	1.205	0.407
$O_2 = 2O(^3P)$	493.6(2)	122.5	465.8	−9.7	1.215	0.523
$C_2 = 2C$	593.1(39)	36.1	570.7	−11.1	1.256	0.285
$O_3 = 3O$	297.5(9)	−130.3	267.0	−19.0	1.264	0.455
$HCl = H + Cl$	427.8(2)	301.2	417.3	−17.3	1.290	0.240
$C_3H_4 = 2CH_2(^3B_1) + C(^5S)$	849.2(22)	542.0	822.8	−53.2	1.307	0.346
$CF_4 = C(^5S) + 4F$	587.8(5)	378.4	572.2	−44.1	1.329	0.294
$C_2H_4 = 2CH_2(^3B_1)$	720.7(42)	452.3	700.8	−42.2	1.331	0.340
$H_2S = 2H + S$	362.2(4)	248.0	351.1	−39.0	1.350	0.211
$C_3H_5 = CH(^4\Sigma^-) + 2CH_2(^3B_1)$	631.2(26)	424.1	613.5	−63.0	1.386	0.309
$C_6H_6 = 6CH(^4\Sigma^-)$	648.4(22)	432.2	628.7	−150.3	1.397	0.305
$F_2 = 2F$	154.6(6)	−158.2	138.9	−6.3	1.403	0.270
$PH_3 = P + 3H$	311.0(7)	216.7	304.8	−62.3	1.425	0.160
$SO_2 = S + 2O$	531.3(2)	184.4	476.3	−17.5	1.464	0.279
$SiH_4 = Si(^5S) + 4H$	416.3(21)	308.6	404.9	−80.7	1.486	0.118
$SiH_3 = Si(^5S) + 3H$	429.1(28)	314.7	416.3	−54.9	1.489	0.117
$OP = O + P$	589.9(34)	226.2	535.2	−7.2	1.499	0.215
cy-$C_3H_6 = 3CH_2(^3B_1)$	367.4(21)	226.5	356.8	−76.0	1.509	0.232
$SiO = Si + O$	794.4(116)	438.0	748.6	−7.3	1.524	0.178
$C_2H_6 = 2CH_3$	369.4(42)	235.1	360.2	−40.1	1.531	0.235
$SF_6 = S + 6F$	324.4(3)	140.0	295.9	−52.5	1.600	0.213
$CCl_4 = C(^5S) + 4Cl$	421.8(5)	239.3	399.9	−24.0	1.793	0.184
$P_2 = 2P$	485.7(29)	143.3	429.1	−4.7	1.905	0.176
$Cl_2 = 2Cl$	239.2	66.6	214.3	−3.1	2.042	0.136
$P_4 = 4P$	299.1(11)	114.2	264.6	−16.0	2.218	0.103
$Si_2H_6 = 2SiH_3$	302.8(64)	219.5	302.6	−17.3	2.351	0.090

[a] Calculated at the B3LYP/6-31G(d) level. [b] Calculated at the bond critical point using the BLYP/6-311+G(d,p) density. 1 au = 6.748×10^{30} m^{-3}. [c] From data in Table 1. Uncertainties $\sigma < 0.05$ kJ/mol are not listed. [d] Using the cc-pVTZ basis sets.

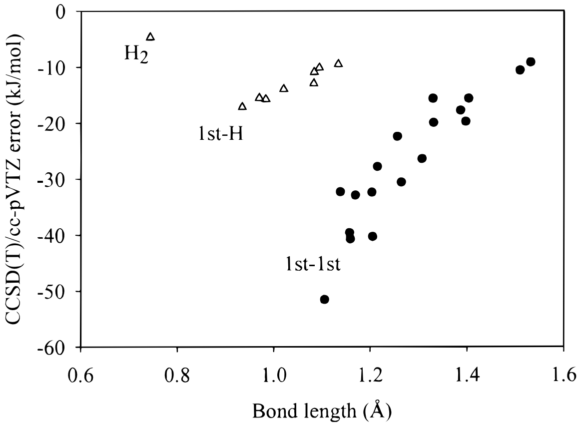

Figure 1. Errors in computed bond strength for first-row compounds, distributed by the length of the breaking bond.

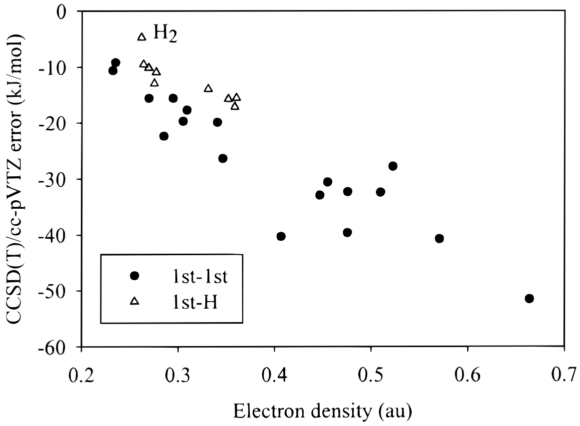

Figure 2. Errors in computed bond strength for first-row compounds, distributed by the electron density at the bond critical point of the breaking bond.

and silicon hydrides.[53] As would be expected from the differing covalent radii of the atoms, the points in Figure 1 are clumped according to the valence principal quantum numbers *n* for the bonded atoms (1−1, 2−1, or 2−2).

The errors in bond strengths are plotted in Figure 2 against the electron density at the bond critical point (i.e., the saddle point in electron density between the bonded atoms). As in Figure 1, bonds involving second-row elements ($n = 3$) are

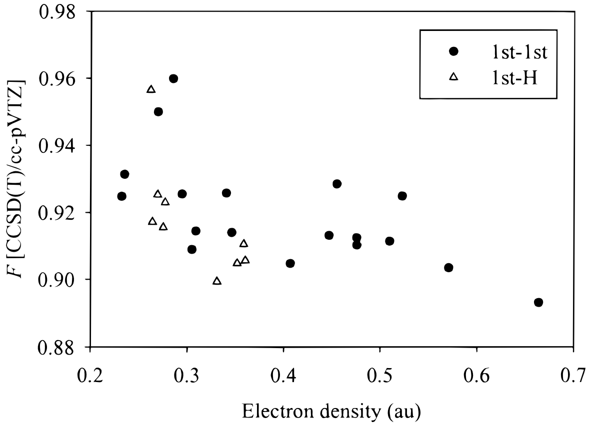

Figure 3. Fraction recovered of the contribution of electron correlation to computed bond strengths (first-row compounds), distributed by the electron density at the critical point of the breaking bond.

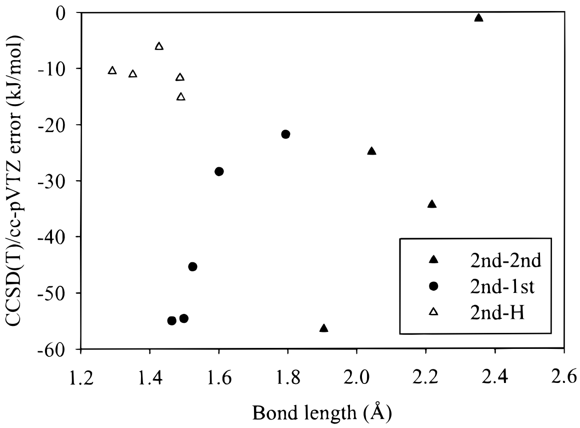

Figure 4. Errors in computed bond strength for second-row compounds, distributed by the length of the breaking bond.

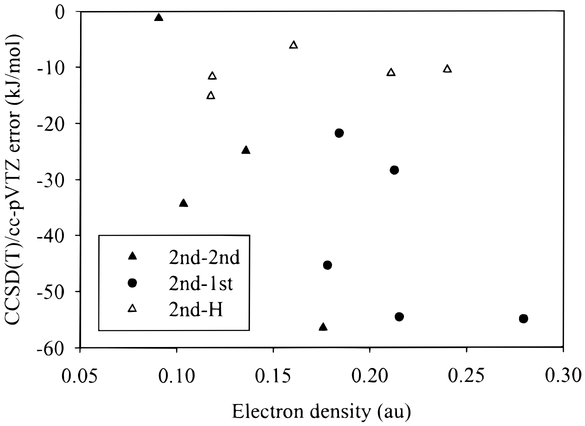

Figure 5. Errors in computed bond strength for second-row compounds, distributed by the electron density at the bond critical point of the breaking bond.

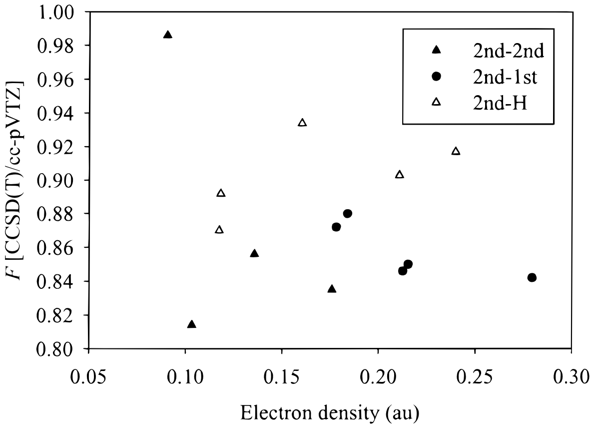

Figure 6. Fraction recovered of the contribution of electron correlation to computed bond strengths (second-row compounds), distributed by the electron density at the critical point of the breaking bond.

excluded for now. Although few bonds appear to have a density ≈0.4 au, all the data lie generally on the same curve.

The fraction *F* of the contribution of electron correlation recovered (eq 1) by the CCSD(T)/cc-pVTZ//B3LYP/6-31G(d) calculations is plotted in Figure 3, again excluding the second-row compounds. The density ρ_b was chosen for the abscissa only to spread the points conveniently. Most of the values of *F* fall between 0.90 and 0.93, but the values for C_2, F_2, and H_2 are noticeably higher, ~0.96.

Bonds involving second-row elements ($n = 3$) are excluded from Figures 1−3 because patterns are less evident. These absolute CCSD(T)/cc-pVTZ errors are plotted in Figure 4 against the corresponding bond lengths and in Figure 5 against electron density. Although these plots show some similarity to Figures 1 and 2 when the principal quantum number of the bonding partner is considered, patterns are less evident. Figure 6 shows the correlation fraction *F*, which is more variable and generally smaller than for the lighter elements. Although more second-row data might reveal more patterns in Figures 4 and 5, the low values of *F* in Figure 6 require explanation (see Discussion).

Errors in bond strength relative to experiment were also calculated at several other levels of theory (HF, B3LYP, MP2, MP4(SDQ), MP4, CCD, and CCSD) and using the smaller 6-31G(d,p) basis sets. Calculations were also done at the B3LYP/6-31G(d), B3LYP/6-311+G(d,p), and MP2/6-31G(d) levels. Tables of bond strengths and plots of their errors analogous to Figures 1−6 are available as Supporting Information. As expected, the smallest errors are found for the CCSD(T) method using the cc-pVTZ basis, which was therefore chosen for further discussion.

Discussion

Inspection of Figures 1−3 shows that all three empirical corrections will provide more robust predictions than can be obtained from purely ab initio calculations. Figures 4−6 indicate that further work will be needed to extend any predictive correlations to second-row energetics. Figures 1 and 4 show that the ab initio error depends more strongly upon the bond length as we descend the periodic table. Thus, error predictions become more sensitive to uncertainties in bond length and are less useful for the heavier elements. The density-based correction looks promising in Figure 2 but nearly worthless for the second-row bonds in Figure 5. Likewise, Figure 3 shows a nearly constant correlation fraction *F*, but there is much more scatter and a different mean value in Figure 6. This suggests that the cc-pVTZ basis sets for the second-row elements [5s,4p,2d,1f] are not correlation balanced with those for the lighter elements [4s,3p,2d,1f], as judged by the criterion of Figures 3 and 6 and of ref 10.

Note that errors in the calculated ZPE contribute to the net errors in bond energies. However, these errors are generally small relative to errors in correlation energy (1 kJ/mol ≈ 84 cm^{-1}), so they are not expected to obscure trends and are absorbed into the empirical corrections described below.

Correlation with Bond Length. In the BAC-MP4 method, the error in the ab initio energies is presumed to depend exponentially upon bond lengths; short, strong bonds are expected to have strong correlation effects that are hard for the ab initio calculations to capture quantitatively. Thus, the CCSD(T)/cc-pVTZ//B3LYP/6-31G(d) data for first-row bonds (Figure 1) can be fitted using eq 2

$$\text{bond energy error} = A \exp(-\alpha r) \tag{2}$$

with different parameters for hydride and for nonhydride bonds. This can be fitted with $A_{12} = -254$ kJ/mol and $\alpha_{12} = 2.87$ Å^{-1} (standard error = 0.8 kJ/mol and maximum error = −1.5 kJ/mol) for bonds between hydrogen and first-row atoms and to $A_{22} = -2448$ kJ/mol and $\alpha_{22} = 3.59$ (standard error = 4.3 kJ/mol and maximum error = 9.0 kJ/mol) for bonds between first-row atoms. The subscripts refer to the valence principal quantum numbers (n) of the two bonded atoms. The (negative) error predicted using eq 2 is subtracted from the calculated bond strength to produce a (larger) corrected bond strength. This is equivalent to adding the predicted error to the energy of the bound molecule. This empirical correction reduces the maximum errors in bond strength predictions by a factor of about 14 for first-row X−H ($n_1 = 2$, $n_2 = 1$) bonds and by a factor of about 7 for first-row X−X ($n_1 = n_2 = 2$) bonds. The BAC-MP4 method has a separate pair of parameters for each pair of bonded elements, supplemented by additional parameters describing substituent effects.[5,54] Fewer parameters are needed here because the present CCSD(T)/cc-pVTZ calculations are much more accurate (and expensive) than are the MP4/6-31G(d,p) calculations underlying BAC-MP4. More refined parameters could be obtained by (1) also applying the energy corrections to any "spectator" bonds that remain in the dissociated fragments, (2) including spin−orbit corrections, (3) using a larger data set that includes multifunctional molecules, (4) considering geometries and ZPEs separately instead of absorbing them in a single empirical correction, (5) weighting the fit to accommodate different uncertainties of the experimental reference data, (6) characterizing the distribution of residual errors (e.g., as Gaussian), (7) including some type of wave function diagnostic, and (8) using better basis sets or a more highly correlated ab initio theory. Such refinements are beyond the scope of this initial report.

Based upon the quality of the fits of the data in Figure 1 to eq 2, the uncertainties in the CCSD(T)/cc-pVTZ bond strengths corrected using eq 2 are $\sigma_{12} = 0.8$ kJ/mol for X−H bonds and $\sigma_{22} = 4.3$ kJ/mol for X−X bonds (standard uncertainties). The corresponding maximum residuals are −1.5 kJ/mol for CH_2 and 9.0 kJ/mol for CO. The residuals for the X−X (i.e., nonhydride) corrections are larger for the molecules requiring larger corrections. Thus, the fractional residuals are more meaningful, and it is better to adopt $\sigma_{22} = 15\%$ of the magnitude of the correction of eq 2 (standard uncertainty). The X−H residuals do not increase particularly with increasing correction, but the uncertainty for the X−H predictions may be expressed fractionally as $\sigma_{12} = 7\%$.

Correlation with Electron Density. Although Figure 2 hints that one might profitably distinguish among the different elements, all the data in the figure can be fitted reasonably well using a single straight line (eq 3). For the CCSD(T)/cc-pVTZ bond energy errors, this yields

$$\text{bond energy error} = a + b(\rho_b) \tag{3}$$

a standard error of 5.8 kJ/mol and a maximum residual of 11.9 kJ/mol ($a = 11$ kJ mol^{-1}, $b = -97$ kJ mol^{-1} bohr^3) [1 bohr^{-3} (atomic unit of electron density) = 6.748 × 10^{30} m^{-3}]. Since all correlation effects must vanish as the density $\rho_b \rightarrow 0$, the apparent nonzero intercept ($a > 0$: overbinding at zero-density limit) is tentatively assigned to basis set superposition error.[55] The correlation of Figure 2 indicates that, as expected, high electron densities are characterized by large correlation energies that are hard to calculate quantitatively. Furthermore, this effect is insensitive to the chemical environment (i.e., the elements involved in the chemical bond). However, the residuals of the fit to eq 3 show approximately linear dependence upon the bond length, with the largest residuals for short bonds (i.e., hydrides). Especially large residuals are associated with bond lengths $r_e \approx 1.2$ Å.

Distinguishing elements from different rows of the periodic table, as done above for bond lengths, leads to improved correlations with electron density. For bonds between hydrogen and first-row elements, the corresponding standard error is 1.0 kJ/mol with a maximum residual of −1.9 kJ/mol ($a_{12} = 5.9$ kJ mol^{-1}, $b_{12} = -61.5$ kJ mol^{-1} bohr^3). For bonds between two first-row atoms, the standard error is 4.9 kJ/mol, and the maximum residual (for acetylene) is 12.5 kJ/mol ($a_{22} = 6.7$ kJ mol^{-1}, $b_{22} = -84.9$ kJ mol^{-1} bohr^3). The correction based upon bond length appears slightly better and is simpler.

Constancy of Contribution of Correlation Energy Recovered. Equation 1 can be rearranged to produce predictions according to eq 4. Choosing the value of F that minimizes the sum of the squared errors from eq 4

$$D_0^{\text{predicted}} = \frac{D_0^{\text{CCSD(T)}} - D_0^{\text{HF}}}{F} + D_0^{\text{HF}} \tag{4}$$

(again excluding H_2 and second-row elements) leads to $F = 0.920$, with a standard error of 6.6 kJ/mol. The three largest errors are 24.1, −14.1, and 10.1 kJ/mol for C_2, N_2, and F_2, respectively. The residuals from this fit vary approximately quadratically with the magnitude of the correction to the Hartree−Fock value, i.e., with the difference $\Delta D_0 = D_0^{\text{predicted}} - D_0^{\text{HF}}$. Thus, the uncertainties for predictions from eq 4 may be expressed as $\sigma = 1.5$ kJ/mol + 3 × 10^{-5} (mol/kJ) × $(\Delta D_0)^2$ (standard error).

Figure 3 suggests that better results would be obtained using a density-dependent value for F as in eq 5.

$$D_0^{\text{predicted}} = \frac{D_0^{\text{CCSD(T)}} - D_0^{\text{HF}}}{F_0 + F_1\rho_b} + D_0^{\text{HF}} \tag{5}$$

Indeed, fitting the same data ($n_1 = 1$ or 2, $n_2 = 2$) yields a standard error of 4.8 kJ/mol with a maximum residual (for C_2) of 13.9 kJ/mol ($F_0 = 0.969$, $F_1 = -0.115$ bohr^3). The errors in the predictions can be approximated as $\sigma = 1.5$ kJ/mol + 0.01 × ΔD_0 (standard error), where ΔD_0 is defined as above.

Other Levels of Theory. Errors in bond strengths calculated at other levels of theory and with the smaller 6-31G(d,p) basis sets can also be examined. In many cases it is profitable simply to add a constant, empirical correction to the calculated bond strengths. For first-row bonds only ($n \leq 2$), the corrections, estimated standard uncertainties, and maximum residuals are compiled in the Supporting Information; the most interesting entries are listed in Table 3. Many of these corrections, especially those involving second-row elements, are tentative and must be corroborated and refined using larger data sets. Nonetheless, several observations can be made.

In contrast to wave function-based theories, B3LYP often overestimates bond strengths. Where the errors do appear to be correlated with r_e or ρ_b, the dependence is weaker for the

TABLE 3: Selected Semiempirical Estimations of X−Y Bond Strengths (Valence Principal Quantum Numbers $n_1 = 1$ or 2, $n_2 = 2$)[a]

correction	method	n_1	param1	param2	stds	max resid	worst
F_0	mp2/cc-pVTZ	2	1.004 (0.997)		15.9 (15.6)	−26.2 (−26.9)	C_3H_4 (O_3)
$a\exp(-br_e)$	mp4(sdq)/6-31g**	1	−682.3	2.76	3.9	5.1	CH_4
$a\exp(-br_e)$	mp4(sdq)/cc-pVTZ	1	−261.3	2.59	1.2	−1.8	$^3CH_2$
$a\exp(-br_e)$	mp4/6-31g**	1	−628.2	2.73	4.1	5.4	CH_4
$a\exp(-br_e)$	mp4/cc-pVTZ	1	−31.3	0.86	1.5	−2.1	$^3CH_2$
F_0	mp4/cc-pVTZ	2	0.967 (0.953)		15.0 (8.4)	49.9 (18.1)	C_2 (O_3)
$a\exp(-br_e)$	mp4/cc-pVTZ	2	−2740.8 (−614.4)	4.36 (2.98)	13.2 (8.0)	41.2 (12.9)	C_2 (CO)
$a + b\rho_b$	mp4/6-31g**	2	33.7 (25.9)	−199.4 (−184.7)	15.4 (13.5)	31.0 (−28.2)	C_2 (C_2H_2)
$a + b\rho_b$	mp4/cc-pVTZ	2	10.0 (1.1)	−55.1 (−38.3)	12.2 (8.1)	35.4 (13.4)	C_2 (O_3)
$a\exp(-br_e)$	ccd/6-31g**	1	−841.2	2.95	3.8	4.6	CH_4
$a\exp(-br_e)$	ccd/cc-pVTZ	1	−460.9	3.09	1.1	−2.0	$^3CH_2$
$F_0 + F_1\rho_b$	ccd/6-31g**	2	0.838 (0.846)	−0.220 (−0.234)	10.9 (10.8)	24.0 (22.2)	F_2 (F_2)
$a\exp(-br_e)$	ccsd/cc-pVTZ	1	−496.4	3.21	0.8	−1.5	$^3CH_2$
$F_0 + F_1\rho_b$	ccsd/cc-pVTZ	2	0.868 (0.889)	−0.082 (−0.123)	5.6 (4.6)	−15.7 (−10.4)	C_2 (O_3)
$a + b\rho_b$	ccsd/cc-pVTZ	2	−5.1 (9.4)	−130.3 (−157.8)	17.6 (9.1)	−57.9 (−17.6)	C_2 (O_3)
$a\exp(-br_e)$	ccsd/6-31g**	2	−7772.4 (−8595.8)	3.66 (3.76)	14.6 (13.9)	32.2 (31.1)	CO (CO)
$a\exp(-br_e)$	ccsd/cc-pVTZ	2	−1850 (−2291.8)	2.76 (2.97)	14.3 (9.6)	−42.1 (−26.0)	C_2 (O_3)
$a\exp(-br_e)$	ccsd(t)/6-31g**	1	−1033.4	3.23	3.5	−4.3	$^3CH_2$
$a\exp(-br_e)$	ccsd(t)/cc-pVTZ	1	−254.2	2.87	0.8	−1.5	$^3CH_2$
$a\exp(-br_e)$	ccsd(t)/6-31g**	2	−14556.5 (−11552.7)	4.46 (4.25)	12.0 (10.6)	26.6 (27.6)	CO (CO)
$a\exp(-br_e)$	ccsd(t)/cc-pVTZ	2	−2447.5 (−2247.0)	3.59 (3.51)	4.3 (4.3)	9.0 (9.1)	CO (CO)
	G2 (ref 33)	1			1.8	4.4	HF
	G2 (ref 33)	2			7.0 (5.1)	24.3 (10.9)	C_2 (HCN)

[a] Base units are kJ/mol, Å, and bohr^{-3}. "stds" refers to the standard error of the fit or the sample standard deviation, "max resid" indicates the worst residual error, and "worst" indicates the corresponding molecule. Parenthetical values indicate results obtained with the C_2 molecule excluded. For the F_0 and $F_0 + F_1\rho_b$ corrections, the parameter values were determined using the combined set $n_1 = 1$ or 2 and not using individual values of n_1.

larger basis sets. The B3LYP error for the C_2 molecule is especially large (−104 kJ/mol using the cc-pVTZ basis), presumably because C_2 has the most severe near-degeneracy problem in the data set; in the CCSD/cc-pVTZ calculation its T_1 diagnostic[56] is 0.039 and its largest t_2 amplitude is 0.286. These quantities are useful gauges of the importance of nondynamic correlation (i.e., multiple configurations). For comparison, the corresponding calculations on the highly correlated molecules O_3 and F_2 yield $T_1 = 0.027$ and 0.010, respectively, and maximal t_2 amplitudes of 0.190 and 0.164, respectively.

Hartree−Fock calculations, the least expensive considered in this study, show the largest errors (always negative). Surprisingly clear trends allow empirical corrections to improve the results dramatically. HF errors obtained using the 6-31G(d,p) and cc-pVTZ basis sets differ surprisingly little, with the largest fractional differences (e.g., 14% for Cl_2) generally for nonhydride bonds involving second-row atoms.

The MP2 results show few trends and several cases of overbinding. They are also quite sensitive to basis set. The largest change in bond strength when the basis is changed from 6-31G(d,p) to cc-pVTZ is +107 kJ/mol for the PO molecule, for which MP2 theory is known to be pathological.[57] The fraction F of correlation contribution recovered (eq 1) is not constant, ranging from 0.73 to 1.07 using the cc-pVTZ basis sets. The lower values of F ($\lesssim 0.90$) are found only for bonds with lower densities, $\rho_b \lesssim 0.3$ au, although many such bonds have high values of F.

The errors found at the MP4(SDQ) level are much more systematic, and empirical corrections are very helpful. Although F still ranges from 0.70 to 0.97 using the cc-pVTZ basis, excluding second-row elements and H_2 leaves a range of 0.82−0.90, with a gentle decline in F as ρ_b increases. The strongest basis set dependence (+78 kJ/mol) is again for the PO diatomic molecule. Full MP4 [i.e., MP4(SDTQ)] shows similar results. Again using the cc-pVTZ basis, F now ranges from 0.85 to 1.05 over the full set of molecules. C_2 is overbound by 30 kJ/mol using this basis set. If second-row elements, H_2, and C_2 are excluded, then F ranges from 0.90 to 0.99, showing little trend with ρ_b. The PO molecule again shows the largest basis set dependence, +101 kJ/mol [cc-pVTZ vs 6-31G(d,p)].

The CCD errors also show useful correlations with r_e and with ρ_b, although among the lighter elements the C_2 molecule does not follow the correlation with density. As in most cases, F lies in a narrower range with the cc-pVTZ basis than with the 6-31G(d,p) basis. Using the larger basis, F ranges from 0.77 to 0.89 (excluding second-row elements and H_2) and is generally smaller for larger values of ρ_b. The strongest basis set dependence is again for PO (+77 kJ/mol).

CCSD results are somewhat better. The corresponding range of F is 0.81−0.90 with a smaller decline with increasing ρ_b than for CCD. The strongest basis set dependence is now for N_2 (+55 kJ/mol); the value for PO is +49 kJ/mol. As expected, the best results are obtained at the CCSD(T) level, for which F ranges from 0.89 to 0.96 (again excluding second-row elements and H_2) and is nearly independent of ρ_b. The strongest basis set dependences are for N_2 (+63 kJ/mol) and for PO (+60 kJ/mol).

Comparison of Methods. Table 4 summarizes the performance of the empirical corrections when applied to the best calculations in this study, CCSD(T)/cc-pVTZ. The results of G2 calculations are also included.[33]

For first-row hydride bonds ($n_1 = 1$, $n_2 = 2$) the corrections based upon bond length and upon electron density yield the best results. Among the other four specific methods, the one based upon both the electron density and the correlation contribution ($F_0 + F_1\rho$) is the least accurate.

For bonds between first-row elements ($n_1 = n_2 = 2$), the comparison depends on whether the anomalous C_2 molecule is included or excluded. When C_2 is included, the correction based upon bond length is the most effective. The two that depend on the density are nearly as good, but the remaining three have errors as large as 24 kJ/mol. When C_2 is excluded from consideration, the smallest errors are obtained using the cor-

TABLE 4: Performance of Empirical Corrections to CCSD(T)/cc-pVTZ X−Y Bond Strengths (n_1 = 1 or 2, n_2 = 2), and of G2 Theory[33,a]

correction	n_1	stds	max resid	worst
constant *a*	1	2.8	−3.9	HF
$a + b\rho_b$	1	1.0	−1.9	$^3CH_2$
$a \exp(-br_e)$	1	0.8	−1.5	$^3CH_2$
F_0	1	2.0	−3.1	NH_3
$F_0 + F_1\rho_b$	1	4.0	−4.7	NH_3
G2 (ref 33)	1	1.8	4.4	HF
constant *a*	2	11.6 (11.9)	−24.5 (−24.3)	N_2 (N_2)
$a + b\rho_b$	2	5.0 (4.9)	−12.5 (−12.8)	C_2H_2 (C_2H_2)
$a \exp(-br_e)$	2	4.3 (4.3)	9.0 (9.1)	CO (CO)
F_0	2	7.9 (5.1)	24.1 (12.4)	C_2 (F_2)
$F_0 + F_1\rho_b$	2	5.3 (3.9)	13.9 (7.8)	C_2 (F_2)
G2 (ref 33)	2	7.0 (5.1)	24.3 (10.9)	C_2 (HCN)

[a] Units are kJ/mol. Headings and methods are as in Table 3.

rection based upon both density and correlation contribution, but the other methods, except for the simple additive constant, are not much inferior.

Other Types of Corrections. Many other schemes have been invented for correcting ab initio energetics. Corrections based upon bond order[58,59] are effective but can be problematic to apply where bond order is not easily determined. Furthermore, since bond order is typically correlated with bond length, with electron density, and with the contribution of correlation energy to bond strength, one might expect any of these other three better-defined quantities to be acceptable surrogates for bond order. Bond-wise corrections based only upon the elements bonded, and not upon bond length, have been successful for a variety of methods.[7] Methods based upon "atom equivalents",[60−65] in which atomic energies are replaced by adjustable parameters for purposes of calculating atomization energies, also incorporate little or no geometric information. Basis set extrapolation methods may involve series of calculations that include no empirical corrections[19,29−31] or may involve analytical extrapolations.[66] All these methods differ in cost, accuracy, and range of applicability and are useful and complementary to the methods evaluated in the present study.

Comparison with G2 Theory. The goal of the present work is to identify useful, systematic patterns in the errors of moderately high-level calculations. All three types of correction reduce the errors in ab initio bond strengths significantly. Further refinement and validation are needed before any of these procedures can be recommended for routine use. Nonetheless, the present, preliminary results can be compared with the popular G2 method, in which empirical corrections are applied to estimated QCISD(T)/6-311+G(3df,2p) energies.[33] As seen in Table 4, the best results from CCSD(T)/cc-pVTZ calculations are achieved using the correction based upon bond length (eq 2). For first-row hydrides ($n_1 = 1$, $n_2 = 2$), the residual errors are about twice as small as those from G2 theory. This is consistent with the quality of basis set for hydrogen atoms ($n = 1$); there are 14 contracted functions in cc-pVTZ but only nine in 6-311+G(2df,2p). For bonds between first-row atoms ($n_1 = n_2 = 2$) the result from eq 2 is also better than G2 theory. This is despite a smaller basis set for first-row atoms ($n = 2$); there are 30 contracted functions in cc-pVTZ but 39 in 6-311+G(3df,2p). This comparison suggests that bond length is a better foundation for an empirical correction than is the spin multiplicity, which is used in G2 theory. However, there are other factors that may contribute to the improvement relative to G2. B3LYP/6-31G(d) geometries and frequencies were used in the present work instead of MP2//HF/6-31G(d) and may be more accurate.[57] Furthermore, QCISD(T) is generally regarded as a less robust approximation to CCSD(T) theory.[67−69] Finally, the G2 parameters were optimized for a different set of molecules than used here.

Although the basis sets are of similar size, G2 calculations are significantly less expensive than the present CCSD(T)/cc-pVTZ calculations. This is because G2 theory involves only an *estimate* of the QCISD(T)/6-311+G(3df,2p) energy; actual calculations at this target level are much more expensive.[70] A similar strategy could be used here to estimate energies and reduce computational cost,[71] but this is beyond the scope of the present study. Such a shortcut might also reduce the accuracy of the predictions, although this was judged not to be a problem in G2 theory.[70]

Conclusions

Three types of empirical correction were compared for correcting ab initio bond energies: (1) exponential in bond length, (2) linear in electron density at the bond critical point, and (3) assuming that the recovered fraction of the total correlation contribution is constant or is linear in electron density at the bond critical point. As expected, empirical corrections are most successful when applied to the highest-level calculations, CCSD(T)/cc-pVTZ. Corrections 1 and 2 are better for bonds to hydrogen ($\sigma \approx 1$ kJ/mol). If the anomalous molecule C_2 is excluded, correction 3 is better for bonds between heavier atoms ($\sigma \approx 4$ kJ/mol for first-row elements). B3LYP and MP2 are somewhat erratic in that their errors appear more random and less systematic than for the higher-level calculations. In many cases, inspection of the residuals can lead to estimates of standard uncertainties that are more reliable than simply using standard deviations or standard errors of fits.

For bonds involving valence principal quantum number $n = 3$ ("second-row" elements, Na−Ar), a smaller fraction of the correlation contribution to the bond energy is recovered than for $n < 3$. This suggests that the cc-pVTZ basis sets are not well balanced across the different rows of the periodic table. Some augmentation will probably be needed (e.g., tight d-functions[72,73]) before these elements can be treated on an equal footing with the lighter elements.

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Supporting Information Available: Computed bond strengths, parameters for corrections to computed bond strengths, and graphs of errors in computed bond strengths appropriate to various correction schemes (64 pages). See any current masthead page for ordering information and Web access instructions.

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