

# Assessment of Experimental Bond Dissociation Energies Using Composite ab Initio Methods and Evaluation of the Performances of Density Functional Methods in the Calculation of Bond Dissociation Energies

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Composite ab initio CBS-Q and G3 methods were used to calculate the bond dissociation energies (BDEs) of over 200 compounds listed in CRC Handbook of Chemistry and Physics (2002 ed.). It was found that these two methods agree with each other excellently in the calculation of BDEs, and they can predict BDEs within 10 kJ/mol of the experimental values. Using these two methods, it was found that among the examined compounds 161 experimental BDEs are valid because the standard deviation between the experimental and theoretical values for them is only 8.6 kJ/mol. Nevertheless, 40 BDEs listed in the Handbook may be highly inaccurate as the experimental and theoretical values for them differ by over 20 kJ/mol. Furthermore, 11 BDEs listed in the Handbook may be seriously flawed as the experimental and theoretical values for them differ by over 40 kJ/mol. Using the 161 cautiously validated experimental BDEs, we then assessed the performances of the standard density functional (DFT) methods including B3LYP, B3P86, B3PW91, and BH&HLYP in the calculation of BDEs. It was found that the BH&HLYP method performed poorly for the BDE calculations. B3LYP, B3P86, and B3PW91, however, performed reasonably well for the calculation of BDEs with standard deviations of about 12.1–18.0 kJ/mol. Nonetheless, all the DFT methods underestimated the BDEs by 4–17 kJ/mol in average. Sometimes, the underestimation by the DFT methods could be as high as 40–60 kJ/mol. Therefore, the DFT methods were more reliable for relative BDE calculations than for absolute BDE calculations. Finally, it was observed that the basis set effects on the BDEs calculated by the DFT methods were usually small except for the heteroatom-hydrogen BDEs.

## 1. INTRODUCTION

Bond dissociation energy (BDE) is defined as the enthalpy change at 298 K and 1 atm for the reaction  $A-B(g) \rightarrow A\cdot(g) + B\cdot(g)$ .<sup>1</sup> A sound knowledge of BDEs is fundamental to understanding chemical processes.<sup>2</sup> Therefore, considerable efforts have been devoted to the development of various methods to determine BDEs.

Gas-phase experiments including radical kinetics, photoionization mass spectrometry, and the acidity/electron affinity cycle are broadly accepted methods for the BDE measurements.<sup>3</sup> Unfortunately, use of these sophisticated methods to determine BDEs of complex molecules remains notoriously hard. In the latest edition of CRC Handbook of Chemistry and Physics, only about 400 BDEs determined using the gas-phase methods are considered to be reliable and, therefore, listed.<sup>4</sup>

Some solution phase experiments using electrochemical or photoacoustic techniques may also be used to determine BDEs.<sup>5</sup> Using these methods one can relatively easily obtain BDEs of a large number of relatively complex molecules. However, because of the solvation effects the BDEs determined using the solution phase methods may be significantly different from the gas-phase BDEs.<sup>6</sup>

The third way to determine BDEs is to use theories. Both the empirical<sup>7</sup> and semiempirical<sup>8</sup> methods may be used to

estimate BDEs, but the ab initio methods are more desirable. Nevertheless, the commonly used Hartree–Fock or perturbation methods are not recommended for BDE calculations due to their spin-contamination problems in dealing with the open-shell systems.<sup>9</sup> More sophisticated ab initio methods such as QCISD and CCSD may perform better than HF and MP2 for the BDE calculations. However, recent studies showed that these more sophisticated methods may still have serious problems with some BDEs.<sup>9</sup>

A more popular theoretical method for the BDE calculations is the density functional theory (DFT).<sup>10</sup> This method usually does not show serious spin-contamination and, therefore, is believed to be desirable for open-shell systems. The relatively low CPU-cost of the DFT method is also advantageous. To date a large number of studies using various DFT methods to calculate BDEs have been reported.<sup>10</sup> Some systematic assessments of the DFT methods for the BDE calculations have also been performed. In 1999, DiLabio et al. showed on the basis of 30 BDEs that the DFT methods can predict BDEs with a mean absolute deviation of about 2 kcal/mol relative to experiment.<sup>11</sup> Korth and Sicking showed on the basis of 15 BDEs that the error of the DFT methods in BDE calculations is about 2.2 kcal/mol.<sup>12</sup> Wiener and Politzer showed on the basis of 28 BDEs that the error of the DFT methods in BDE calculations is less than 2.5 kcal/mol.<sup>13</sup> In contrast to these results, Jursic reported that BDEs computed using DFT methods may be substantially lower (5–10 kcal/mol) than the experimental values.<sup>14</sup> Our recent studies also showed that the DFT method

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**Table 1.** Experimental and Theoretical BDEs (kJ/mol)

compound	exp	CBS-Q	G3	theor <sup>a</sup>	B3LYP/ 6-31G(d)	B3LYP/ 6-311++ G(d,p)	B3LYP/ 6-311++ G(3df,2p)	B3P86/ 6-311++ G(d,p)	B3PW91/ 6-311++ G(d,p)	BH&HLYP/ 6-311++ G(d,p)
H-CH <sub>3</sub>	438.9 ± 0.4	439.2	435.7	437.4	438.9	430.2	430.9	441.5	426.3	422.7
H-CCH	556.1 ± 2.9	557.2	558.3	557.8	556.3	562.6	563.6	571.0	554.2	558.6
H-CHCH <sub>2</sub>	465.3 ± 3.4	461.6	461.0	461.3	456.9	452.5	453.1	462.9	447.6	449.9
H-C <sub>2</sub> H <sub>5</sub>	423.0 ± 1.6	425.1	422.9	424.0	419.3	414.1	411.4	422.2	407.3	406.7
H-CH <sub>2</sub> CCH	374.0 ± 8	380.0	381.5	380.8	366.7	364.4	364.1	376.3	362.3	364.3
H-CH <sub>2</sub> CHCH <sub>2</sub>	361.9 ± 8.8	361.0	363.3	362.2	355.6	350.8	350.5	362.2	348.1	346.1
H-Cyclopropyl	444.8 ± 1.3	449.9	448.8	449.4	444.9	441.2	441.5	452.2	437.1	439.7
H- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	423.3 ± 2.1	426.5	424.2	425.4	420.4	414.2	412.4	423.2	408.3	407.9
H- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	409.1 ± 2.0	414.6	413.5	414.0	402.9	396.5	396.2	407.0	392.1	394.1
H-Cyclobutyl	403.8 ± 4	421.6	420.6	421.1	406.9	401.7	401.1	412.2	397.1	399.7
H-Cyclopropylmethyl	407.5 ± 6.7	410.6	409.5	410.0	407.3	398.9	398.7	410.7	396.1	397.6
H-CH(CH <sub>3</sub> )CHCH <sub>2</sub>	345.2 ± 5.4	350.0	354.0	352.0	340.2	336.5	335.9	347.1	332.8	334.4
H-CH <sub>2</sub> CHCHCH <sub>3</sub> (trans)	358.2 ± 6.3	360.2	362.7	361.4	353.4	348.2	348.3	359.8	345.8	344.7
H-CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub>	358.2 ± 4	364.1	367.3	365.7	360.4	355.2	354.7	367.3	352.8	350.9
H- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	425.4 ± 2.1	427.2	425.2	426.2	421.2	413.7	413.9	424.9	409.9	409.6
H- <i>i</i> -C <sub>4</sub> H <sub>9</sub>	425.2 ± 2.1	427.7	425.6	426.6	421.6	413.6	413.4	424.6	409.6	409.2
H- <i>s</i> -C <sub>4</sub> H <sub>9</sub>	411.2 ± 2.0	416.1	414.5	415.3	403.9	397.4	397.0	408.0	393.0	395.2
H- <i>t</i> -C <sub>4</sub> H <sub>9</sub>	404.3 ± 1.3	408.8	407.3	408.0	389.4	385.3	384.5	395.7	380.4	384.9
H-Cyclopenta-1,3-dien-5-yl	346.7	345.8	348.4	347.1	333.4	332.9	332.7	344.3	330.4	328.2
H-Cyclopent-1-en-3-yl	344.3 ± 4	347.1	352.0	349.6	339.0	334.9	334.1	345.4	331.4	332.9
H-CH <sub>2</sub> CHCHCHCH <sub>2</sub>	347 ± 13	333.2	340.6	336.9	330.5	325.7	325.0	337.5	323.8	321.1
H-CH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	319.7	301.7	311.5	306.6	292.6	292.4	291.4	303.1	289.4	291.3
H-CH(CH <sub>3</sub> )CCCH <sub>3</sub>	365.3 ± 11.3	377.9	375.0	376.4	349.0	347.4	346.6	358.3	344.3	350.0
H-Cyclopentyl	403.5 ± 2.5	403.7	402.7	403.2	384.5	379.5	379.3	389.4	374.9	376.2
H-CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	418.8 ± 8	432.0	428.9	430.4	423.5	416.4	416.1	427.4	412.3	412.1
H-C(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	404.0 ± 6.3	405.0	404.0	404.5	385.3	381.5	380.5	392.7	376.9	381.5
H-C <sub>6</sub> H <sub>5</sub>	473.1 ± 3.0	480.1	484.1	482.1	463.2	462.0	462.1	472.2	456.7	461.5
H-Cyclohexa-1,3-dien-5-yl	305 ± 21	305.7	317.1	311.4	299.1	296.7	296.2	307.5	293.7	294.3
H-Cyclohexa-1,4-dien-3-yl	305.4 ± 8.4	307.6	316.2	311.9	298.4	296.5	296.5	307.6	294.1	296.6
H-Cyclohexyl	399.6 ± 4	417.4	415.7	416.6	405.0	398.3	397.9	409.5	394.4	396.5
H-C(CH <sub>3</sub> ) <sub>2</sub> CCCH <sub>3</sub>	344.3 ± 11.3		364.4		336.3	335.9	334.7	346.4	332.1	339.8
H-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	375.7 ± 1.7	376.4	380.8	378.6	367.1	362.0	361.5	374.6	360.7	358.2
H-Cycloheptyl	387.0 ± 4		408.8		398.9	393.3	392.8	404.1	389.3	391.5
H-CN	527.6 ± 1.7	534.5	536.6	535.6	531.9	539.2	539.6	549.7	533.9	550.1
H-CH <sub>2</sub> CN	392.9 ± 8.4	401.2	401.7	401.4	388.8	386.5	385.7	398.9	384.6	384.7
H-CH <sub>2</sub> NC	380.7 ± 8.8	399.4	399.5	399.4	386.3	384.3	382.8	395.0	380.7	384.7
H-CH(CH <sub>3</sub> )CN	376.1 ± 9.6	386.2	386.7	386.4	368.7	366.7	366.1	378.1	363.9	367.2
H-C(CH <sub>3</sub> ) <sub>2</sub> CN	361.9 ± 8.4	373.2	375.4	374.3	352.1	350.6	349.7	361.6	347.2	353.0
H-CH <sub>2</sub> NH <sub>2</sub>	390.4 ± 8.4	390.0	389.0	389.5	383.0	374.4	374.9	385.6	371.4	374.1
H-CHO	368.5 ± 1.0	370.0	369.4	369.7	364.4	359.9	360.2	372.1	357.7	361.8
H-CHCO	440.6 ± 8.8	444.1	448.5	446.3	431.8	432.5	432.5	445.8	431.4	435.0
H-COCH <sub>3</sub>	373.8 ± 1.5	373.5	373.7	373.6	367.9	363.1	363.2	375.5	360.9	365.3
H-COCHCH <sub>2</sub>	364.4 ± 4.2	380.8	381.2	381.0	372.5	368.4	368.8	380.5	365.7	370.7
H-COC <sub>2</sub> H <sub>5</sub>	371.3	373.9	374.6	374.2	368.5	363.6	363.7	376.3	361.5	366.0
H-COCF <sub>3</sub>	380.7 ± 8	388.1	388.8	388.4	378.2	376.9	376.2	388.9	374.1	381.4
H-CH <sub>2</sub> CHO	394.6 ± 9.2	401.2	398.8	400.0	386.8	383.9	384.3	396.7	382.5	379.0
H-CH <sub>2</sub> COCH <sub>3</sub>	411.3 ± 7.5	405.7	402.4	404.0	391.6	389.0	389.4	401.5	387.1	384.7
H-CH(CH <sub>3</sub> )COCH <sub>3</sub>	386.2 ± 5.9	385.2	383.5	384.4	365.1	363.4	363.2	374.7	360.7	362.4
H-CH <sub>2</sub> OCH <sub>3</sub>	402.2	404.4	402.9	403.6	398.0	390.4	390.2	401.9	387.2	390.1
H-CH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	383.7 ± 1.7	401.4	400.9	401.2	391.0	385.9	383.6	396.3	381.6	386.3
H-tetrahydrofuran-2-yl	385 ± 4	391.8	391.6	391.7	380.2	376.1	375.5	386.7	372.1	377.2
H-CH <sub>2</sub> OH	401.8 ± 1.5	404.2	402.5	403.4	395.5	390.7	390.2	401.6	387.0	389.5
H-CH(CH <sub>3</sub> )OH	401.4	398.1	397.5	397.8	385.3	381.7	380.8	391.9	377.2	381.6
H-CH(OH)CHCH <sub>2</sub>	341.4 ± 7.5	328.4	332.1	330.2	317.1	315.8	313.0	325.5	311.2	317.2
H-C(CH <sub>3</sub> ) <sub>2</sub> OH	381 ± 4	394.6	394.9	394.8	377.8	375.3	374.0	385.4	370.2	376.7
H-CH <sub>2</sub> F	423.8 ± 4	425.2	423.3	424.2	413.2	413.2	412.2	423.5	408.6	410.5
H-CHF <sub>2</sub>	431.8 ± 4	426.6	425.7	426.2	409.8	413.9	411.8	423.8	408.7	414.5
H-CF <sub>3</sub>	449.5	447.5	447.3	447.4	429.8	434.2	431.4	444.8	429.1	437.1
H-CHFCI	421.7 ± 5.4	415.3	414.7	415.0	403.6	404.9	401.8	414.5	399.7	404.9
H-CF <sub>2</sub> CI	421.3 ± 8.3	426.8	426.8	426.8	410.7	414.5	411.3	425.1	409.9	416.6
H-CFCl <sub>2</sub>	413.8 ± 5.0	409.6	409.0	409.3	395.2	397.8	393.2	408.2	393.2	399.3
H-CH <sub>2</sub> Cl	419.0 ± 2.3	417.8	415.2	416.5	411.3	405.7	402.7	415.4	400.8	403.1
H-CHCl <sub>2</sub>	402.5 ± 2.7	402.7	401.5	402.1	395.6	393.8	389.0	402.8	388.3	393.2
H-CH <sub>2</sub> CH <sub>2</sub> Cl	423.1 ± 2.4	427.1	424.9	426.0	416.3	409.5	410.2	422.5	407.8	408.7
H-CH(CH <sub>3</sub> )Cl	406.6 ± 1.5	410.5	408.7	409.6	401.3	397.3	394.0	406.6	391.9	395.8
H-C(CH <sub>3</sub> )Cl <sub>2</sub>	390.6 ± 1.5	400.9	398.8	399.8	388.0	387.2	382.2	396.5	381.5	386.8
H-CCl <sub>3</sub>	392.5 ± 2.5	393.6	391.3	392.4	380.7	381.8	375.4	390.9	376.2	381.5
H-CH <sub>2</sub> -CF <sub>3</sub>	446.4 ± 4.6	447.0	443.7	445.4	436.8	432.0	432.3	443.3	428.2	428.5
H-CFCH <sub>3</sub>	416.3 ± 10.5	424.5	424.0	424.2	407.1	409.1	406.3	419.1	403.7	410.4
H-C <sub>2</sub> F <sub>5</sub>	429.7 ± 2.1	440.2	435.5	437.8	416.0	418.8	414.4	429.0	413.4	422.6
H-CHClCF <sub>3</sub>	425.9 ± 6.3	419.4	417.6	418.5	408.0	404.3	400.6	414.6	399.8	405.7
H-CCl <sub>2</sub> CHCl <sub>2</sub>	393 ± 8	394.1	393.4	393.8	392.9	391.8	385.1	401.9	386.9	393.7

Table 1 (Continued)

compound	exp	CBS-Q	G3	theor <sup>a</sup>	B3LYP/ 6-31G(d)	B3LYP/ 6-311++ G(d,p)	B3LYP/ 6-311++ G(3df,2p)	B3P86/ 6-311++ G(d,p)	B3PW91/ 6-311++ G(d,p)	BH&HLYP/ 6-311++ G(d,p)
H-CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	415.1 ± 4	425.7	423.1	424.4	416.5	413.5	413.2	425.7	410.9	407.5
H-CH <sub>2</sub> SH	392.9 ± 8.4	399.7	398.0	398.8	399.5	390.9	386.7	401.4	387.3	389.9
H-CH <sub>2</sub> SCH <sub>3</sub>	384.9 ± 5.9	393.6	392.7	393.2	394.6	385.0	380.3	395.8	381.9	385.5
H-NH <sub>2</sub>	452.7 ± 1.3	449.6	446.3	448.0	425.3	437.9	438.0	452.6	436.3	425.6
H-NHCH <sub>3</sub>	418.4 ± 10.5	418.3	416.4	417.4	371.7	401.7	401.7	416.1	400.3	393.8
H-N(CH <sub>3</sub> ) <sub>2</sub>	382.8 ± 8	395.0	393.9	394.4	369.3	376.4	376.3	390.8	375.3	370.6
H-NHC <sub>6</sub> H <sub>5</sub>	368.2 ± 8	368.6	384.0	376.3	358.0	368.4	369.3	384.7	370.2	363.2
H-NO	195.4 ± 0.2	199.9	198.5	199.2	190.0	195.4	196.1	207.2	192.3	184.5
H-NF <sub>2</sub>	316.7 ± 10.5	303.1	308.6	305.8	281.6	298.8	298.6	309.6	293.9	295.6
H-OH	497.0 ± 0.4	497.5	493.2	495.4	457.7	480.2	484.4	496.5	479.0	459.4
H-OCH <sub>3</sub>	436.0 ± 3.8	441.4	439.4	440.4	397.8	415.4	418.0	430.6	414.0	404.3
H-OC <sub>2</sub> H <sub>5</sub>	437.7 ± 3.4	444.5	442.5	443.5	403.1	421.9	424.4	437.4	420.7	411.3
H-OC(CH <sub>3</sub> ) <sub>3</sub>	439.7 ± 4	446.3	446.3	446.3	403.5	421.4	422.3	437.5	420.5	411.8
H-OCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	428.0 ± 6.3	444.2	438.1	441.2	398.4	417.7	418.0	433.2	416.5	411.3
H-OC <sub>6</sub> H <sub>5</sub>	361.9 ± 8	357.7	368.7	363.2	331.3	347.2	350.8	364.4	349.2	344.5
H-OOH	369.0 ± 4.2	367.7	362.6	365.2	324.6	345.7	346.1	356.9	340.9	339.0
H-OOCH <sub>3</sub>	370.3 ± 2.1	357.8	355.9	356.8	320.7	337.4	338.6	349.4	333.5	333.8
H-OCOCH <sub>3</sub>	442.7 ± 8	459.9	461.4	460.6	416.4	433.1	434.3	448.8	432.5	460.3
H-ONO	327.6 ± 2.1	325.0	326.7	325.8	297.9	313.8	312.9	320.4	304.7	325.7
H-SiH <sub>3</sub>	384.1 ± 2.0	386.1	383.2	384.6	376.7	375.6	377.6	380.6	366.0	377.0
H-SiH <sub>2</sub> CH <sub>3</sub>	374.9	389.8	387.4	388.6	379.2	377.8	380.1	383.0	368.3	380.4
H-SiH(CH <sub>3</sub> ) <sub>2</sub>	374.0	393.7	391.7	392.7	382.3	380.6	383.0	385.9	371.2	384.2
H-Si(CH <sub>3</sub> ) <sub>3</sub>	377.8	396.7	395.4	396.0	385.3	383.1	385.5	388.5	373.7	387.3
H-SiF <sub>3</sub>	418.8	435.2	422.2	428.7	414.4	403.5	408.8	409.9	395.0	412.3
H-SiCl <sub>3</sub>	382.0	392.9	387.2	390.0	368.7	367.6	371.2	376.7	362.5	377.4
H-Si <sub>2</sub> H <sub>5</sub>	361.1	373.7	371.5	372.6	365.0	364.0	365.3	369.4	355.0	365.3
H-PH <sub>2</sub>	351.0 ± 2.1	345.1	341.2	343.2	334.5	335.6	338.6	346.0	331.8	330.8
H-SH	381.6 ± 2.9	382.2	377.5	379.8	362.2	368.1	373.7	382.5	368.1	359.5
H-SCH <sub>3</sub>	365.3 ± 2.5	363.8	360.4	362.1	340.8	347.9	352.0	360.5	346.4	341.2
H-SC <sub>6</sub> H <sub>5</sub>	348.5 ± 8	366.3	365.2	365.8	306.6	315.7	322.1	330.4	317.0	311.5
CH <sub>3</sub> -CH <sub>3</sub>	376.0 ± 2.1	376.5	369.4	373.0	373.1	353.2	352.7	371.1	360.0	343.4
CH <sub>3</sub> -CH <sub>2</sub> CCH	318.0 ± 8	326.3	324.7	325.5	306.1	292.3	290.7	310.9	300.7	290.2
CH <sub>3</sub> -CH(CH <sub>3</sub> )CCH	305.4	326.9	322.4	324.6	293.6	280.5	279.1	299.2	288.2	280.8
CH <sub>3</sub> -CH <sub>2</sub> CHCHCH <sub>3</sub>	305.0 ± 3.3	311.7	307.2	309.4	292.8	276.3	274.7	295.1	284.7	270.9
CH <sub>3</sub> -CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub>	301.2 ± 3.3	311.1	309.8	310.4	296.2	279.4	278.5	299.3	288.4	273.4
CH <sub>3</sub> -CH(CH <sub>3</sub> )CCCH <sub>3</sub>	320.9 ± 6.3		322.7		291.6	278.4	277.1	297.1	286.2	279.6
CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	284.9 ± 6.3	305.6	303.2	304.4	270.2	256.6	254.8	276.6	264.3	256.1
<i>n</i> -C <sub>3</sub> H <sub>7</sub> -CH <sub>2</sub> CHCH <sub>2</sub>	295.8	313.5	307.5	310.5	280.2	264.3	262.4	283.7	272.3	261.7
CH <sub>3</sub> -CN	509.6 ± 8	516.9	513.8	515.4	516.8	509.6	510.6	528.3	516.6	517.9
C <sub>2</sub> H <sub>5</sub> -CH <sub>2</sub> NH <sub>2</sub>	332.2 ± 8	345.2	340.6	342.9	320.4	371.2	299.0	318.8	307.5	300.8
CH <sub>3</sub> -CH <sub>2</sub> CN	336.4 ± 4	349.7	345.0	347.4	328.5	314.8	313.0	333.9	323.4	311.1
CH <sub>3</sub> -CH(CH <sub>3</sub> )CN	329.7 ± 8	345.0	338.5	341.8	311.7	298.4	297.0	317.5	306.4	297.6
CH <sub>2</sub> F-CH <sub>2</sub> F	368 ± 8	388.8	384.3	386.6	368.4	355.2	351.7	370.8	359.5	355.4
CH <sub>3</sub> -CF <sub>3</sub>	423.4 ± 4.6	434.8	431.0	432.9	413.5	400.6	397.3	418.1	405.5	403.2
CF <sub>3</sub> -CF <sub>3</sub>	413.0 ± 10.5	416.1	416.5	416.3	390.5	362.2	363.8	380.7	366.7	373.0
CH <sub>2</sub> CHCH <sub>2</sub> -Si(CH <sub>3</sub> ) <sub>3</sub>	293		323.3	-	276.1	269.5	271.1	285.9	275.1	273.9
CH <sub>3</sub> -N <sub>2</sub> CH <sub>3</sub>	219.7	222.4	221.9	222.2	211.3	199.7	200.2	219.5	207.6	191.8
C <sub>2</sub> H <sub>5</sub> -N <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	209.2	225.5	225.9	225.7	202.4	262.2	190.0	210.7	198.5	186.7
CH <sub>3</sub> -NO	167.4 ± 3.3	162.9	158.9	160.9	161.6	150.1	151.8	167.1	155.6	133.8
<i>i</i> -C <sub>3</sub> H <sub>7</sub> -NO	152.7 ± 13	169.9	168.5	169.2	148.7	139.6	140.0	157.0	144.7	129.1
<i>t</i> -C <sub>4</sub> H <sub>9</sub> -NO	165.3 ± 6.3	177.8	171.2	174.5	140.9	132.5	132.2	152.0	138.4	124.0
CF <sub>3</sub> -NO	179.1 ± 8	171.5	168.4	170.0	157.7	140.0	143.1	158.1	145.6	132.2
CCl <sub>3</sub> -NO	134 ± 13	133.5	128.9	131.2	106.0	98.0	95.1	117.0	104.6	77.8
CH <sub>3</sub> -NO <sub>2</sub>	254.4	251.8	250.6	251.2	236.5	228.9	228.6	246.8	234.3	234.5
<i>i</i> -C <sub>3</sub> H <sub>7</sub> -NO <sub>2</sub>	246.9	265.4	266.9	266.2	230.4	222.6	221.2	241.6	227.9	235.0
CH <sub>3</sub> -OC(CH <sub>3</sub> )CH <sub>2</sub>	277.4	269.2	262.7	266.0	243.3	228.4	232.5	247.1	233.5	221.5
CH <sub>3</sub> -SH	312.5 ± 4.2	313.8	304.2	309.0	295.3	282.8	288.5	303.1	293.2	269.5
C <sub>6</sub> H <sub>5</sub> -SH	361.9 ± 8	383.4	377.7	380.6	336.9	329.5	337.4	351.8	340.8	319.6
CH <sub>3</sub> -SCH <sub>3</sub>	307.9 ± 3.3	308.1	300.4	304.2	282.5	271.2	276.6	290.7	280.6	260.1
F-CH <sub>3</sub>	472	465.0	458.7	461.8	454.2	442.0	453.3	457.7	443.3	406.2
F-CF <sub>2</sub> CH <sub>3</sub>	522.2 ± 8	539.9	536.3	538.1	526.7	495.0	508.5	515.3	499.4	470.4
Cl-CN	421.7 ± 5.0	439.7	435.8	437.8	416.7	415.5	432.1	439.4	428.8	408.4
Cl-CF <sub>3</sub>	360.2 ± 3.3	372.2	365.5	368.8	335.8	328.3	337.2	351.6	340.0	315.9
Cl-CHFCI	354.4 ± 11.7	347.9	339.8	343.8	308.1	305.1	311.8	326.6	315.7	289.0
Cl-CF <sub>2</sub> Cl	346.0 ± 13.4	351.6	345.1	348.4	307.3	303.5	311.7	327.2	315.7	289.5
Cl-CFCl <sub>2</sub>	305 ± 8	330.5	321.6	326.0	278.2	276.7	283.8	300.1	288.6	261.0
Cl-CH <sub>2</sub> Cl	350.2 ± 0.8	340.3	330.4	335.4	305.4	300.2	305.6	320.3	310.0	283.1
Cl-CHCl <sub>2</sub>	338.5 ± 4.2	325.7	314.5	320.1	278.6	277.7	282.7	298.5	287.7	260.3
Cl-CCl <sub>3</sub>	305.9 ± 7.5	309.2	294.7	302.0	245.5	246.1	253.4	268.5	257.0	228.2
Cl-SiCl <sub>3</sub>	464	476.2	463.5	469.8	405.4	400.2	421.7	423.5	413.2	401.4
NH <sub>2</sub> -NH <sub>2</sub>	275.3	276.1	268.2	272.2	260.6	256.5	254.1	278.8	265.6	233.2
NH <sub>2</sub> -NHCH <sub>3</sub>	268.2 ± 8	269.8	263.0	266.4	246.1	240.4	238.3	262.7	249.3	221.4

Table 1 (Continued)

compound	exp	CBS-Q	G3	theor <sup>a</sup>	B3LYP/ 6-31G(d)	B3LYP/ 6-311++ G(d,p)	B3LYP/ 6-311++ G(3df,2p)	B3P86/ 6-311++ G(d,p)	B3PW91/ 6-311++ G(d,p)	BH&HLYP/ 6-311++ G(d,p)
NH <sub>2</sub> -N(CH <sub>3</sub> ) <sub>2</sub>	246.9 ± 8	267.3	260.3	263.8	237.4	227.9	226.1	251.6	237.5	210.9
HO-NO	206.3	209.4	201.2	205.3	206.5	191.0	198.1	213.5	200.3	138.2
HO-NO <sub>2</sub>	206.7	205.0	201.7	203.4	200.6	181.3	189.7	206.4	192.4	158.5
HO <sub>2</sub> -NO <sub>2</sub>	96 ± 8	100.0	98.7	99.4	84.4	71.6	76.9	91.7	79.0	47.5
CH <sub>3</sub> O-NO	174.9 ± 3.8	183.4	177.1	180.2	168.4	147.4	154.9	171.4	157.6	105.0
C <sub>2</sub> H <sub>5</sub> O-NO	175.7 ± 5.4	185.6	178.9	182.2	171.5	151.4	159.4	176.0	162.2	110.2
<i>n</i> -C <sub>3</sub> H <sub>7</sub> O-NO	167.8 ± 7.5	182.9	177.1	180.0	159.1	145.1	150.5	169.9	166.1	119.8
<i>i</i> -C <sub>3</sub> H <sub>7</sub> O-NO	171.5 ± 5.4	182.5	175.1	178.8	148.7	128.6	134.7	153.7	139.3	88.8
<i>n</i> -C <sub>4</sub> H <sub>9</sub> O-NO	177.8 ± 6.3	183.4	177.1	180.2	158.4	144.3	149.7	167.9	155.0	118.3
<i>i</i> -C <sub>4</sub> H <sub>9</sub> O-NO	175.7 ± 6.3	184.8	176.6	180.7	157.7	144.7	164.3	167.0	153.4	101.1
<i>s</i> -C <sub>4</sub> H <sub>9</sub> O-NO	173.6 ± 3.3	192.0	182.7	187.4	161.3	148.2	159.0	173.7	158.4	122.5
<i>t</i> -C <sub>4</sub> H <sub>9</sub> O-NO	171.1 ± 3.3	183.4	178.1	180.8	157.7	145.4	148.6	169.1	155.2	104.6
HO-OH	213 ± 4	212.0	201.4	206.7	207.8	184.2	193.2	203.0	188.5	128.3
HO-OCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	193.7 ± 7.9	184.7	176.9	180.8	170.7	149.8	155.6	166.8	152.6	106.5
CH <sub>3</sub> O-OCH <sub>3</sub>	157.3 ± 8	169.9	162.9	166.4	139.8	118.3	124.3	134.0	119.9	79.1
C <sub>2</sub> H <sub>5</sub> O-OC <sub>2</sub> H <sub>5</sub>	158.6 ± 4	176.0	168.5	172.2	146.5	121.9	129.4	140.0	125.1	84.1
HO-Cl	251 ± 13	238.9	229.0	234.0	212.3	197.1	220.9	215.6	203.3	151.1
HO-Si(CH <sub>3</sub> ) <sub>3</sub>	536	557.3	550.8	554.0	509.5	497.0	514.1	509.8	494.9	488.4
HS-SH	276 ± 8	269.2	257.6	263.4	230.8	222.8	246.8	244.9	236.0	203.8
CH <sub>3</sub> S-SCH <sub>3</sub>	272.8 ± 3.8	270.9	263.6	267.2	217.0	213.6	233.5	234.2	224.9	196.8
H <sub>3</sub> Si-SiH <sub>3</sub>	310	316.9	317.9	317.4	298.1	292.2	294.9	303.4	295.8	295.5

<sup>a</sup> BDE (theor) = 1/2 (BDE (G3) + BDE (CBS-Q)).

may estimate the BDEs to various extents.<sup>15</sup> Since not all of these studies fully agree with each other, a more comprehensive assessment of the performances of the DFT methods in BDE calculations is still needed.

At present, the most reliable way to calculate BDEs is to use the composite ab initio methods such as G3 and CBS-Q, which have been shown to be able to predict BDEs within 1–2 kcal/mol of the experimental values.<sup>9</sup> Unfortunately, the composite ab initio calculation usually costs a great deal of CPU time. As a result, although a number of BDEs calculated using the composite ab initio methods have been compared with the experimental values in recent studies,<sup>9,16</sup> no one has examined the reliability of the composite ab initio methods in the calculation of BDEs using a sample containing more than 50 compounds.

The original purpose of the present study is to assess the performances of the composite ab initio and DFT methods for the BDE calculations using much more experimental BDEs than the previous studies. However, after we completed the calculations, we found that not all the experimental BDEs are trustworthy. Therefore, to obtain more reliable information we performed detailed statistical analyses. On the basis of the analyses, we first validated the use of composite ab initio methods for the BDE calculations because of the excellent agreement for the majority cases. Then we singled out those experimental BDEs whose values are very different from the values predicted by the composite ab initio methods. These experimental BDEs were deemed questionable, and the possible origins of their errors were discussed. Finally, using the majority experimental BDEs which agree excellently with the composite ab initio methods, we examined the performances of the DFT methods for the BDE calculations.

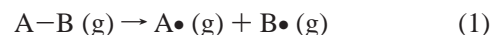
## 2. METHOD

All the experimental data were taken from CRC Handbook of Chemistry and Physics.<sup>4</sup> Only the molecules with less than

eight non-hydrogen atoms were considered in this study because of the limitation of CPU resources. Using this criterion we established a database containing about 200 compounds (Tables 1 and 2).

The calculations were done using Gaussian 98.<sup>17</sup> Geometry optimization was conducted without any constraint. Each optimized structure was confirmed by the frequency calculation to be the real minimum without any imaginary vibration frequency. To find the optimal conformation for each compound, a search of various conformers was conducted using UB3LYP/6-31G(d) method. The optimal conformation from the search was used as the starting geometry for the G3 or CBS-Q calculation. For the DFT calculations, we always used the B3LYP/6-31G(d) geometry.

BDEs were calculated using composite ab initio G3 and CBS-Q methods or DFT B3LYP/6-31G(d), B3LYP/6-311++G(d,p), B3LYP/6-311++G(3df,2p), B3P86/6-311++G(d,p), B3PW91/6-311++G(d,p), and BH&HLYP/6-311++G(d,p) methods, as the enthalpy change of the following reaction in the gas phase at 298 K, 1 atm.



The enthalpy of formation for each species was calculated using the following equation:

$$H_{298} = E + ZPE + H_{trans} + H_{rot} + H_{vib} + RT \quad (2)$$

ZPE is the zero point energy.  $H_{trans}$ ,  $H_{rot}$ , and  $H_{vib}$  are the standard temperature correction term calculated using the equilibrium statistical mechanics with harmonic oscillator and rigid rotor approximations.<sup>18</sup> It is worthy to note that for the DFT methods, zero point energies and temperature corrections were calculated at B3LYP/6-31G(d) level scaled by 0.9804.<sup>19</sup>

It should be mentioned that the composite ab initio methods involve a series of calculations that are designed to recover the errors that result from the truncation of both the one-electron basis set and the number of configurations



**Table 2.** Compounds for Which the Difference between the Theoretical and Experimental BDEs Are Larger than 20 kJ/mol

compounds	exp	CBS-Q <sup>a</sup>	G3	theor
H-Cycloprop-2-en-1-yl	379.1 ± 1.7	420.8	419.6	420.2
H-CH(CH <sub>3</sub> )CCH	347.7 ± 9.2	366.8	370.6	368.7
H-C(CH <sub>3</sub> ) <sub>2</sub> CCH	338.9 ± 9.6	360.6	363.8	362.2
H-C(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	323.0 ± 6.3	341.6	346.7	344.2
H-CH <sub>2</sub> C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub>	326.4 ± 4.6	356.7	359.8	358.2
H-C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub>	319.2 ± 4.6	345.0	355.7	350.4
H-CH <sub>2</sub> NHCH <sub>3</sub>	364 ± 8	387.7	387.1	387.4
H-CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	351 ± 8	387.8	387.7	387.8
H-COOCH <sub>3</sub>	387.9 ± 4	417.4	417.7	417.6
H-CHCF <sub>2</sub>	448 ± 8	492.6	492.5	492.6
H-CFCHF	448 ± 8	481.1	483.1	482.1
H-CFCF <sub>2</sub>	452 ± 8	492.4	494.1	493.2
H-CFCFCI	444 ± 8	485.5	487.7	486.6
HCCICFCI	439 ± 8	472.2	474.0	473.1
H-CCICHCi	435 ± 8	462.4	465.2	463.8
H-CHCICHCH <sub>2</sub>	370.7 ± 5.9	348.5	352.7	350.6
H-NO <sub>2</sub>	327.6 ± 2.1	290.0	293.5	291.8
H-NHNH <sub>2</sub>	366.1	342.8	343.7	343.2
H-NH <sub>3</sub> <sup>+</sup>	385 ± 21	522.6	518.7	520.6
H-OOC(CH <sub>3</sub> ) <sub>3</sub>	374.0 ± 0.8	349.6	350.3	350.0
H-OCOC <sub>2</sub> H <sub>5</sub>	445.2 ± 8	477.3	473.6	475.4
H-ONO <sub>2</sub>	423.4 ± 2.1	446.4	444.2	445.3
H-SiH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	369.0	402.0	384.8	393.4
CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> CCH	295.8 ± 6.3	330.1	321.8	326.0
n-C <sub>3</sub> H <sub>7</sub> -CH <sub>2</sub> CCH	306.3 ± 6.3	334.9	326.7	330.8
C <sub>2</sub> H <sub>5</sub> -CH <sub>2</sub> CN	321.7 ± 7.1	350.4	345.9	348.2
CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> CN	312.5 ± 6.7	339.0	333.4	336.2
NC-CN	536 ± 4	584.5	585.9	585.2
CH <sub>3</sub> CO-COCH <sub>3</sub>	282.0 ± 9.6	312.7	309.6	311.2
NC-NO	120.5 ± 10.5	211.5	211.8	211.6
CH <sub>2</sub> C(CH <sub>3</sub> )-NO <sub>2</sub>	245.2	300.8	294.6	297.7
t-C <sub>4</sub> H <sub>9</sub> -NO <sub>2</sub>	244.8	269.4	268.3	268.8
t-C <sub>4</sub> H <sub>9</sub> -SH	286.2 ± 6.3	319.1	309.1	314.1
F-CN	469.9 ± 5.0	522.5	521.9	522.2
F-COF	535 ± 12	512.4	509.7	511.0
F-CHFCI	465.3 ± 9.6	500.0	496.1	498.0
F-CF <sub>2</sub> Cl	490 ± 25	520.2	516.8	518.5
F-CFCl <sub>2</sub>	462.3 ± 10.0	486.5	483.6	485.0
Cl-CSCl	265.3 ± 2.1	330.2	325.4	327.8
HO-NCHCH <sub>3</sub>	207.9	261.7	254.6	258.2

<sup>a</sup> BDE (theor) = 1/2 (BDE (G3) + BDE (CBS-Q)).

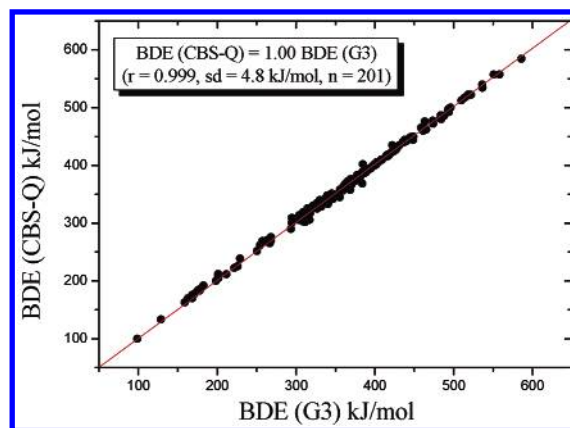
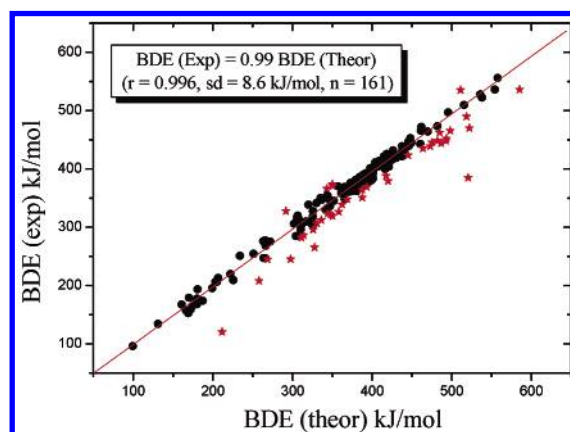
used for treating correlation energies. G3 (Gaussian-3, G3/MP2)<sup>20</sup> is one of the composite ab initio methods, whose geometry optimization is done at MP2(full)/6-31G(d) level. A scaled HF/6-31G(d) ZPE is used in G3. A base energy calculated at MP4/6-31G(d) level is then corrected to QCISD(T)(full)/G3Large level using several additivity approximations at MP2 and MP4 levels, to take account of more complete incorporation of electron correlation, core correlation, and the effect of a large basis set. The root-mean-square-error in the calculation of atomization energies by G3 is 1.21 kcal/mol.

CBS-Q is another composite ab initio method.<sup>21</sup> It starts with HF/6-31G\* geometry optimization and frequency calculation, which is then followed by the MP2(FC)/6-31G\* optimization. The single-point energy is calculated at MP2/6-311+G(3d2f, 2df, 2p), MP4(SDQ)/6-31+G(d(f),p), and QCISD(T)/6-31+G\* levels. This energy is then extrapolated to the complete basis set limit. The root-mean-square-error in the calculation of atomization energies by CBS-Q is 1.42 kcal/mol.

### 3. RESULTS AND DISCUSSION

#### 3.1. Reliability of the Composite ab initio Methods.

Over 200 compounds with less than eight non-hydrogen

**Figure 1.** The correlation between the BDEs calculated using CBS-Q and G3 methods.**Figure 2.** The correlation between the experimental and theoretical BDEs. The data shown by the red stars are not included in the correlation.

atoms are examined in the present study (see Tables 1 and 2). The chemical bonds undergoing homolysis include C-H, N-H, O-H, Si-H, P-H, S-H, C-C, C-Si, C-N, C-O, C-S, C-F, C-Cl, Si-Cl, N-N, N-O, O-O, O-Cl, O-Si, S-S, and Si-Si. The highest BDE is that for H-CCH, 556.1 kJ/mol. The lowest BDE is that for HO<sub>2</sub>-NO<sub>2</sub>, 96 kJ/mol.

Two different composite ab initio methods, CBS-Q and G3, are used to calculate BDEs. The correlation between the BDEs calculated by the two methods is shown in Figure 1. According to Figure 1, the agreement between the two composite ab initio methods is excellent for the BDEs of 201 compounds. The correlation coefficient is 0.999. The standard deviation is 4.8 kJ/mol. It should be mentioned that such a good agreement is remarkable because the G3 and CBS-Q methods use different strategies in the extrapolation to complete incorporation of electron correlation and complete basis set limit. Also, since these two methods provide very similar results, we use the average values of the CBS-Q and G3 BDEs as the theoretical BDEs for the further analyses.

Comparing the theoretical and experimental BDEs (Figure 2), we find that for 161 compounds the agreement between the theory and experiment is good. The correlation coefficient is 0.996. The standard deviation is 8.6 kJ/mol. Since the experimental error (see Table 1) for the BDE measurements is often as large as 10 kJ/mol, the good agreement between the theory and experiment indicates that we can trust the composite ab initio methods in predicting BDEs. Also, the

good agreement between the theory and experiment indicates that the 161 experimental BDE values are valid.

**3.2. Possible Experimental Errors.** Despite the excellent agreement between the theory and experiment for the majority cases, we find that the experimental and theoretical BDEs differ by over 20 kJ/mol for 40 compounds (see Table 2). Since the disagreement between the theory and experiment for most cases is much smaller than 20 kJ/mol, the BDEs for the 40 compounds compiled in the handbook are likely inaccurate. It is worthy to note that an error of 20 kJ/mol is serious for the strength of a chemical bond.

Furthermore, the experimental and theoretical BDEs differ by over 40 kJ/mol for 11 compounds in Table 2. This magnitude of difference indicates that these experimental data were wrongly estimated, or the theoretical calculations were seriously flawed. To find out which is the case, in the following we perform more detailed examinations on these 11 compounds.

H-cycloprop-2-en-1-yl: The experimental BDE is  $379.1 \pm 17$  kJ/mol, but the theoretical BDE is 420.2 kJ/mol. It was calculated earlier that the C<sub>1</sub>–H BDE for cyclopropene should be about 7 kcal/mol (or ~28 kJ/mol) smaller than that for cyclopropane.<sup>22</sup> Since the C<sub>1</sub>–H BDE for cyclopropane is 444.8 kJ/mol (exp) or 449.4 kJ/mol (theor), we conclude that the experimental C<sub>1</sub>–H BDE for cyclopropene is invalid.

H–CHCF<sub>2</sub>: The experimental BDE as listed in the handbook<sup>4</sup> is  $448 \pm 8$  kJ/mol. However, the experimental BDE from the original reference is  $110 \pm 2$  kcal/mol (or  $460 \pm 8$  kJ/mol).<sup>23</sup> Nevertheless, both the values are smaller than the C–H BDE of ethylene (465.3 kJ/mol (exp) or 461.3 kJ/mol (theor)) and, therefore, are not reasonable. The theoretical BDE we obtained is 492.6 kJ/mol. The theoretical BDE obtained by Zhang using the CBS-4 method was 118.2 kcal/mol (or 494.5 kJ/mol).<sup>24</sup> Thus, the experimental BDE was significantly underestimated. The same problem occurred for H–CFCF<sub>2</sub> and H–CFCFCl.

H–NH<sub>3</sub><sup>+</sup>: The experimental BDE is  $385 \pm 21$  kJ/mol, which is about 135 kJ/mol smaller than the theoretical BDE (520.6 kJ/mol). According to a recent estimation on the basis of gas-phase proton affinity and adiabatic ionization potential, the N–H BDE of NH<sub>4</sub><sup>+</sup> should fall between 123.6 and 127.9 kcal/mol (or 517–535 kJ/mol).<sup>25</sup> Clearly, our theoretical BDE is correct.

NC–CN: The experimental BDE listed in the handbook is  $536 \pm 4$  kJ/mol. The recent experimental BDE for the same bond is 563.6 kJ/mol.<sup>26</sup> This value is close to our theoretical value, 585.2 kJ/mol.

NC–NO: The experimental BDE listed in the handbook is  $120.5 \pm 10.5$  kJ/mol. Zewail et al. recently reported that the BDE of NC–NO was 48.8 kcal/mol (or 204 kJ/mol).<sup>27</sup> This value is close to our theoretical BDE, 211.6 kJ/mol.

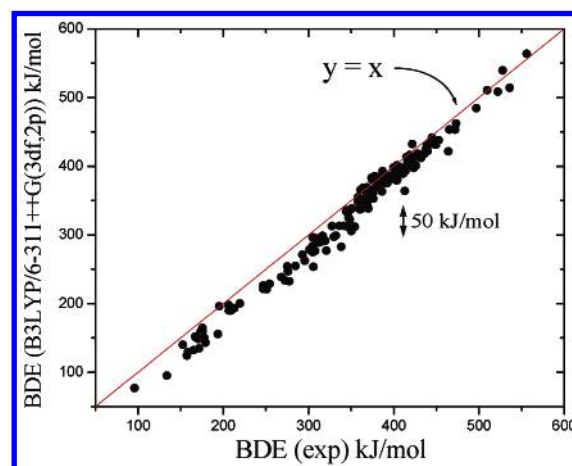
CH<sub>2</sub>C(CH<sub>3</sub>)–NO<sub>2</sub>: The experimental BDE is 245.2 kJ/mol. Our theoretical value is 297.7 kJ/mol. It should be noted that the C–N BDE of C<sub>6</sub>H<sub>5</sub>–NO<sub>2</sub> is about 71 kcal/mol (or 297 kJ/mol).<sup>28</sup> This indicates that our theoretical value is more reasonable.

F–CN: The experimental BDE is 469.9 kJ/mol. Our theoretical value is 522.2 kJ/mol. Cl–CSCl: The experimental BDE is 265.3 kJ/mol. Our theoretical value is 327.8 kJ/mol. HO–NCHCH<sub>3</sub>: The experimental BDE is 207.9 kJ/mol. Our theoretical value is 258.2 kJ/mol. There is no other

**Table 3.** Correlation Analyses on the DFT BDEs for All the Compounds<sup>a</sup>

method	correlation slope	correlation coefficient	SD (kJ/mol)	mean error (kJ/mol)
B3LYP/6-31G(d)	0.964	0.988	15.4	–14.0
B3LYP/6-311++G(d,p)	0.956	0.987	18.1	–17.6
B3LYP/6-311++G(3df,2p)	0.958	0.993	14.5	–16.8
B3P86/6-311++G(d,p)	0.991	0.992	12.2	–4.0
B3PW91/6-311++G(d,p)	0.954	0.993	12.9	–17.8
BH&HLYP/6-311++G(d,p)	0.942	0.983	27.4	–25.3

<sup>a</sup> The correlation equation is  $\text{BDE (theor)} = k \times \text{BDE (exp)}$ .



**Figure 3.** Underestimation of the experimental BDEs by the DFT methods.

study which can help us judge which values are more reasonable for the above three cases.

**3.3. Performances of the DFT Methods.** Using the 161 validated experimental BDEs in Table 1, we can assess the performances of the DFT methods for BDE calculations. The detailed analysis results are shown in Table 3.

According to Table 3, all the DFT methods except for BH&HLYP/6-311++G(d,p) can modestly well predict the BDEs. The slopes of the correlations are from 0.954 to 0.991. They are lower than unity indicating that all the DFT methods systematically underestimate the BDEs. This finding is in agreement with Jursic's<sup>14</sup> and our<sup>15</sup> previous observations. Further analyses indicate that the mean underestimation is about 14.0–17.8 kJ/mol (i.e. 3.3–4.2 kcal/mol) for most of the DFT methods. Such a magnitude of underestimation can also be seen evidently in Figure 3. One particular method, B3P86/6-311++G(d,p), has an underestimation of 4.0 kJ/mol (or 1.0 kcal/mol) only. The correlation coefficients for all the DFT BDEs are from 0.987 to 0.993, which are excellent. The standard deviations, 12.2–18.1 kJ/mol (i.e. 2.9–4.3 kcal/mol), are slightly larger than those reported by DiLabio et al.,<sup>11</sup> Korth and Sicking,<sup>12</sup> and Wiener and Politzer.<sup>13</sup>

Interestingly, from Table 3 one may find that the basis set effects on the performance of the DFT methods in BDE calculations are not large. In fact, although the B3LYP/6-311++G(3df,2p) results are slightly better than those from B3LYP/6-31G(d) in the correlation coefficient and standard deviation, the B3LYP/6-311++G(d,p) results are worse than the B3LYP/6-31G(d) results. The small basis set effects on DFT methods are to be expected because in DFT methods

**Table 4.** Correlation Analyses on the DFT BDEs for C–H Bonds<sup>a</sup>

method	correlation slope	correlation coefficient	SD (kJ/mol)	mean error (kJ/mol)
B3LYP/6-31G(d)	0.983	0.981	8.4	−6.8
B3LYP/6-311++G(d,p)	0.976	0.985	7.9	−9.9
B3LYP/6-311++G(3df,2p)	0.973	0.985	8.2	−11.1
B3P86/6-311++G(d,p)	1.002	0.985	7.7	+1.0
B3PW91/6-311++G(d,p)	0.966	0.985	7.9	−13.7
BH&HLYP/6-311++G(d,p)	0.974	0.981	9.0	−10.8

<sup>a</sup> The correlation equation is  $\text{BDE (theor)} = k \times \text{BDE (exp)}$ .

the electron correlation is treated by the functional rather than through electron excitation as in conventional ab initio methods.

**3.3.1. C–H Bonds.** The performances of the DFT methods in the BDE calculations for every subset of chemical bonds have also been analyzed. The first and largest subset in our analyses is the C–H bond. This subset contains 72 compounds. The correlation analysis results for this subset are shown in Table 4.

Comparing Table 4 with Table 3, one can see that the DFT methods perform much better for C–H bonds than for all the chemical bonds. The standard deviations for the DFT C–H BDEs are about 7–9 kJ/mol (or 1.7–2.2 kcal/mol). The average underestimations are about 6.8–13.7 kJ/mol (or 1.6–3.3 kcal/mol) for B3LYP, B3PW91, and BH&HLYP methods, whereas B3P86/6-311++G(d,p) actually shows a slight overestimation of the C–H BDEs by 1.0 kJ/mol. In addition, from the results for B3LYP/6-31G(d), B3LYP/6-311++G(d,p), and B3LYP/6-311++G(3df,2p) one can see that the basis set effects on the calculated C–H BDEs are very small.

A few important BDEs in this subset and their corresponding to theoretical values are shown in the following. From these typical systems, one can see again that the DFT methods can predict the C(sp<sup>3</sup>)-H, C(sp<sup>2</sup>)-H, and C(sp)-H BDEs reasonably well.

CH<sub>3</sub>-H: 438.9 ± 0.4 (exp.), 438.9 (B3LYP/6-31G(d)), 430.2 (B3LYP/6-311++G(d,p)), 430.9 (B3LYP/6-311++G(3df,2p)), 441.5 (B3P86/6-311++G(d,p)), 426.3 (B3PW91/6-311++G(d,p)), and 422.7 (BH&HLYP/6-311++G(d,p)).

CH<sub>2</sub>CH-H: 465.3 ± 3.4 (exp.), 456.9 (B3LYP/6-31G(d)), 452.5 (B3LYP/6-311++G(d,p)), 453.1 (B3LYP/6-311++G(3df,2p)), 462.9 (B3P86/6-311++G(d,p)), 447.6 (B3PW91/6-311++G(d,p)), and 449.9 (BH&HLYP/6-311++G(d,p)).

HCC-H: 556.1 ± 2.9 (exp.), 556.3 (B3LYP/6-31G(d)), 562.6 (B3LYP/6-311++G(d,p)), 563.6 (B3LYP/6-311++G(3df,2p)), 571.0 (B3P86/6-311++G(d,p)), 554.2 (B3PW91/6-311++G(d,p)), and 558.6 (BH&HLYP/6-311++G(d,p)).

**3.3.2. Heteroatom-H Bond.** The second subset is for the heteroatom (i.e. N, O, Si, P, S)-H bonds. This subset contains 25 compounds. The correlation analysis results are shown in Table 5.

From Table 5, it is interesting to see that the basis set effects on the heteroatom-H BDEs are significant. From 6-31G(d) to 6-311++G(3df,2p) both the standard deviation and mean error decrease drastically. These strong basis set effects can also be seen from Table 1. According to Table 1, from 6-31G(d) to 6-311++G(3df,2p) the calculated O–H BDE of H<sub>2</sub>O increases from 457.7 to 484.4 kJ/mol.

**Table 5.** Correlation Analyses on the DFT BDEs for Heteroatom-H Bonds<sup>a</sup>

method	correlation slope	correlation coefficient	SD (kJ/mol)	mean error (kJ/mol)
B3LYP/6-31G(d)	0.941	0.951	16.8	−22.2
B3LYP/6-311++G(d,p)	0.968	0.983	10.0	−12.3
B3LYP/6-311++G(3df,2p)	0.973	0.984	9.8	−10.2
B3P86/6-311++G(d,p)	0.998	0.987	9.1	−0.5
B3PW91/6-311++G(d,p)	0.959	0.986	9.2	−15.9
BH&HLYP/6-311++G(d,p)	0.961	0.961	15.3	−14.9

<sup>a</sup> The correlation equation is  $\text{BDE (theor)} = k \times \text{BDE (exp)}$ .

**Table 6.** Correlation Analyses on the DFT BDEs for C–X Bonds<sup>a</sup>

method	correlation slope	correlation coefficient	SD (kJ/mol)	mean error (kJ/mol)
B3LYP/6-31G(d)	0.946	0.986	17.0	−18.9
B3LYP/6-311++G(d,p)	0.921	0.972	22.5	−26.6
B3LYP/6-311++G(3df,2p)	0.920	0.990	16.6	−27.8
B3P86/6-311++G(d,p)	0.969	0.990	13.4	−10.8
B3PW91/6-311++G(d,p)	0.934	0.990	14.8	−22.6
BH&HLYP/6-311++G(d,p)	0.890	0.979	21.6	−37.4

<sup>a</sup> The correlation equation is  $\text{BDE (theor)} = k \times \text{BDE (exp)}$ .

With the 6-311++G(d,p) basis set, the B3LYP, B3P86, B3PW91, and BH&HLYP methods all show a standard deviation of 9–15 kJ/mol. They all underestimate the heteroatom-H BDEs by about 12–16 kJ/mol except for the B3P86 method. B3P86/6-311++G(d,p) only shows an underestimation of 0.5 kJ/mol.

A few important BDEs in this subset and their corresponding to theoretical values are shown in the following. From these typical systems, one can see again that the DFT methods seriously underestimate the heteroatom-H BDEs by about 5 kcal/mol.

NH<sub>2</sub>-H: 452.7 ± 1.3 (exp.), 425.3 (B3LYP/6-31G(d)), 437.9 (B3LYP/6-311++G(d,p)), 438.0 (B3LYP/6-311++G(3df,2p)), 452.6 (B3P86/6-311++G(d,p)), 436.3 (B3PW91/6-311++G(d,p)), and 425.6 (BH&HLYP/6-311++G(d,p)).

HO-H: 497.0 ± 0.4 (exp.), 457.7 (B3LYP/6-31G(d)), 480.2 (B3LYP/6-311++G(d,p)), 484.4 (B3LYP/6-311++G(3df,2p)), 496.5 (B3P86/6-311++G(d,p)), 479.0 (B3PW91/6-311++G(d,p)), and 459.4 (BH&HLYP/6-311++G(d,p)).

HS-H: 381.6 ± 2.9 (exp.), 362.2 (B3LYP/6-31G(d)), 368.1 (B3LYP/6-311++G(d,p)), 373.7 (B3LYP/6-311++G(3df,2p)), 382.5 (B3P86/6-311++G(d,p)), 368.1 (B3PW91/6-311++G(d,p)), and 359.5 (BH&HLYP/6-311++G(d,p)).

**3.3.3. C–X (X ≠ H) Bonds.** The third subset is for the C–X (X ≠ H) bonds. There are 39 compounds in this subset. The bonds include C–C, C–N, C–O, C–F, C–Cl, C–Si, and C–S. The correlation analysis results are shown in Table 6.

According to Table 6, the performances of the DFT methods on the C–X bonds are much less satisfactory than the performances of the DFT methods on the C–H bonds. The standard deviations are about 13.4–22.5 kJ/mol. The mean underestimations are as large as 19–37 kJ/mol except for the B3P86/6-311++G(d,p). B3P86/6-311++G(d,p) shows an underestimation of 10.8 kJ/mol.

It is worthy to note that for the C–X bonds, the basis set effects on the calculated BDEs are irregular. In fact,



**Table 7.** Correlation Analyses on the DFT BDEs for X–Y Bonds<sup>a</sup>

method	correlation slope	correlation coefficient	SD (kJ/mol)	mean error (kJ/mol)
B3LYP/6-31G(d)	0.916	0.989	13.2	−19.3
B3LYP/6-311++G(d,p)	0.869	0.991	15.0	−33.3
B3LYP/6-311++G(3df,2p)	0.907	0.996	11.6	−24.2
B3P86/6-311++G(d,p)	0.945	0.990	13.0	−12.1
B3PW91/6-311++G(d,p)	0.899	0.990	13.6	−24.8
BH&HLYP/6-311++G(d,p)	0.775	0.984	34.4	−62.7

<sup>a</sup> The correlation equation is BDE (theor) =  $k \times$  BDE (exp).

comparing B3LYP/6-31G(d), B3LYP/6-311++G(d,p), and B3LYP/6-311++G(3df,2p) results one may find that B3LYP/6-31G(d) gives the best results among the three.

A typical compound which can show all the problems about the DFT performances indicated by the correlation analyses in this subset is CH<sub>3</sub>–CH<sub>3</sub>. As shown in the following, B3LYP/6-31G(d) fortuitously provides a value close to the experimental BDE. However, B3LYP/6-311++G(d,p) and B3LYP/6-311++G(3df,2p) both show an underestimation of about 5 kcal/mol. B3P86/6-311++G(d,p)'s BDE is close to the experimental result, whereas BH&HLYP/6-311++G(d,p) shows an underestimation of about 8 kcal/mol.

CH<sub>3</sub>–CH<sub>3</sub>: 376.0 ± 2.1 (exp.), 373.1 (B3LYP/6-31G(d)), 353.2 (B3LYP/6-311++G(d,p)), 352.7 (B3LYP/6-311++G(3df,2p)), 371.1 (B3P86/6-311++G(d,p)), 360.0 (B3PW91/6-311++G(d,p)), and 343.4 (BH&HLYP/6-311++G(d,p)).

**3.3.4. X–Y (X,Y ≠ C or H) Bonds.** The last subset is for the X–Y (X,Y ≠ C or H) bonds. There are 24 compounds in this subset. The bonds include N–N, N–O, O–O, O–Cl, O–Si, O–S, Si–Si, S–S, and Si–Cl. The correlation analysis results are shown in Table 7.

According to Table 7, the standard deviations of the calculated BDEs are about 11–15 kJ/mol except for the BH&HLYP/6-311++G(d,p) method. The mean underestimations are about 12–33 kJ/mol except for BH&HLYP/6-311++G(d,p). BH&HLYP/6-311++G(d,p) performs unacceptably poorly with the X–Y (X,Y ≠ C or H) bonds. Its standard deviation is 34.4 kJ/mol (or 8.2 kcal/mol). Its mean error is −62.7 kJ/mol (or −15.0 kcal/mol).

**3.3.5. Summary Remarks about the DFT Methods.** The above results and analyses show that the DFT methods are reasonably reliable for the BDE calculations. However, underestimation of the BDEs is always a problem for the DFT methods, and the magnitude of underestimation varies from system to system. Sometimes, the underestimation is so large that one should not trust the absolute BDEs from the DFT calculations. A good example for this situation is the Cl–Si BDE in SiCl<sub>4</sub>. The experimental BDE is 464 kJ/mol, but the BDEs from the B3LYP/6-31G(d), B3LYP/6-311++G(d,p), B3LYP/6-311++G(3df,2p), B3P86/6-311++G(d,p), B3PW91/6-311++G(d,p), and BH&HLYP/6-311++G(d,p) calculations are 405.4, 400.2, 421.7, 423.5, 413.2, and 401.4 kJ/mol. All the calculated values are about 10–15 kcal/mol smaller than the experimental result.

Despite the underestimation problem, correlation analyses have shown that the DFT BDEs are in good correlation with the experimental BDEs, especially when very similar chemical bonds are taken into consideration. This means that the

BDE underestimation by the DFT methods is mostly systematic. Therefore, one can use the DFT method to calculate the relative BDEs in a closely related group reliably. Then, by choosing the smallest compound in the group and conducting a composite ab initio calculation to get the absolute BDE for this particular compound, one will be able to get reliable absolute BDEs for the whole group using the relative BDEs.<sup>29</sup>

For certain reason to be clarified the half-and-half hybrid BH&HLYP functional performs the worst among the several standard DFT methods for the BDE calculations. Therefore, we do not recommend the use of BH&HLYP for the calculation of BDEs. On the other hand, although the B3P86 functional mostly shows the smallest underestimation of the BDEs, we do not suggest that B3P86 should be much more reliable than the other DFT methods for BDE calculations. In fact, according to Tables 3–7 the standard deviation of B3P86 in the BDE calculations is as large as the standard deviations for the other DFT methods, indicating that their results are of similar trustworthiness.

#### 4. CONCLUSION

An enormous amount of theoretical computation was performed in order to examine the reliability of the composite ab initio methods and DFT methods in predicting BDEs. It was found that the composite CBS-Q and G3 methods excellently agree with each other in the calculation of BDEs, and these two methods can predict BDEs within 10 kJ/mol of the experimental values. Using these two methods, it was found that 40 BDEs documented in CRC Handbook of Chemistry and Physics are significantly inaccurate, and 11 BDEs of them may be seriously flawed.

Using the validated experimental BDEs, we then assessed the performances of the standard density functional (DFT) methods including B3LYP, B3P86, B3PW91, and BH&HLYP in the calculation of BDEs. It was found that the BH&HLYP method performed poorly for the BDE calculations. B3LYP, B3P86, and B3PW91, however, performed reasonably well for the calculation of BDEs with standard deviations of about 12.1–18.0 kJ/mol. Nonetheless, all the DFT methods underestimated the BDEs by 4–17 kJ/mol in average. Sometimes, the underestimation by the DFT methods could be as high as 40–60 kJ/mol. Therefore, the DFT methods were more reliable for relative BDE calculations than for absolute BDE calculations.

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**Supporting Information Available:** Structures of the compounds whose experimental and theoretical BDEs differ by over 20 kJ/mol (Table 1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (18) It should be mentioned that the method we used to calculate BDEs at 298 K, 1 atm is exactly the same as that used by Wright et al. (See: DiLabio, G. A.; Pratt, D. A.; LoFaro, A. D.; Wright, J. S. *J. Phys. Chem. A* **1999**, *103*, 1653.) In fact, using B3LYP/6-31G(d), Wright et al. obtained  $H^\circ_{298}(\text{H}_2\text{O}) = -76.38401$  hartree,  $H^\circ_{298}(\text{OH}) = -75.71185$  hartree,  $H^\circ_{298}(\text{H}) = -0.49791$  hartree, and BDE ( $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ ) = 109.3 kcal/mol. In comparison, our data are  $H^\circ_{298}(\text{H}_2\text{O}) = -76.384007$  hartree,  $H^\circ_{298}(\text{OH}) = -75.711846$  hartree,  $H^\circ_{298}(\text{H}) = -0.497912$ , and BDE ( $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ ) = 109.3 kcal/mol.
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