

G3//BMK and Its Application to Calculation of Bond Dissociation Enthalpies

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Abstract: On the basis of systematic examinations it was found that the BMK functional significantly outperformed the other popular density functional theory methods including B3LYP, B3P86, KMLYP, MPW1P86, O3LYP, and X3LYP for the calculation of bond dissociation enthalpies (BDEs). However, it was also found that even the BMK functional might dramatically fail in predicting the BDEs of some chemical bonds. To solve this problem, a new composite *ab initio* method named G3//BMK was developed by combining the strengths of both the G3 theory and BMK. G3//BMK was found to outperform the G3 and G3//B3LYP methods. It could accurately predict the BDEs of diverse types of chemical bonds in various organic molecules within a precision of *ca.* 1.2 kcal/mol.

1. Introduction

Bond dissociation enthalpy (BDE) is defined as the enthalpy change of the gas-phase reaction $A-B \rightarrow A\cdot + B\cdot$ at 298 K, 1 atm.¹ A sound knowledge of BDE is fundamental to understanding diverse chemical and biochemical processes.² For that reason, there have been considerable efforts devoted to the determination of BDEs of various molecules.³ Nonetheless, because of the experimental difficulties in dealing with highly reactive radical species, it remains difficult to reliably measure the BDEs of many important compounds. Much controversy has also taken place in the literature over the past 20 years concerning the BDEs of some simple molecules.³

An alternative approach to obtain BDE is to use quantum chemistry theories. This approach has proven to be useful and important in many fields because it is fast and relatively inexpensive. However, because open-shell radical systems are involved, one should be careful to choose theoretical methods for BDE calculation. Generally speaking, unrestricted Hartree–Fock and perturbation methods are not recommended for BDE calculation due to their spin-contamination problems.⁴ More sophisticated *ab initio* methods such as QCISD and CCSD tend to outperform HF and MP2, but these advanced methods may also seriously underestimate some BDEs.⁵

The density functional theory (DFT) is currently a more practicable method for BDE calculation.^{6,7} 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. Nevertheless, Jursic's⁸ and our previous studies⁹ showed that some popular DFT methods tend to underestimate BDEs by *ca.* 2–6 kcal/mol! This conclusion was supported by several more recent studies.¹⁰ Some of the latest studies also showed from a more general perspective that popular DFT models (e.g., B3LYP) could systematically underestimate various reaction energies in treatments of organic molecules.^{11,12}

The reliability problem of the DFT methods calls for the development and performance test of new functionals for each particular computational target.¹³ Here we report on the basis of systematic tests that the newly developed BMK functional considerably outperforms many other popular functionals including B3LYP, B3P86, KMLYP, MPW1P86, O3LYP, and X3LYP for the BDE calculation. From this finding we further develop a new composite *ab initio* method named G3//BMK. This new method can accurately and reliably predict the BDEs of diverse types of chemical bonds in various organic molecules within a precision of *ca.* 1.2 kcal/mol. All calculations were performed with the Gaussian 03 suite of programs.¹⁴

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Table 1. Correlation between the Experimental BDEs and Theoretical Predictions by Different DFT Methods^c

compound	exp ^a	B3LYP ^b	B3P86 ^b	KMLYP ^b	X3LYP ^b	O3LYP ^b	MPW1P86 ^b	BMK ^b
CH ₃ –CH ₃	90.2 ± 0.2	84.2	88.5	93.2	84.8	85.1	87.9	90.1
CH ₃ –C ₂ H ₅	88.5 ± 0.5	81.2	85.5	91.3	81.9	81.6	85.3	88.6
CH ₃ – <i>n</i> C ₃ H ₇	88.9 ± 0.7	81.4	85.7	91.6	82.1	81.7	85.5	88.5
CH ₃ – <i>i</i> C ₃ H ₇	88.2 ± 0.9	78.4	82.8	89.7	79.3	78.0	82.9	86.6
CH ₃ – <i>n</i> C ₄ H ₉	88.8 ± 0.7	81.3	85.6	91.5	82.0	81.6	85.4	88.8
CH ₃ –C≡CH	126.5 ± 1.0	124.1	128.3	134.7	124.8	123.6	128.1	129.7
C ₂ H ₅ –C≡CH	124.5 ± 1.0	120.7	124.7	131.9	121.5	119.7	124.8	127.2
CH ₃ –CH=CH ₂	101.9 ± 1.5	94.8	99.2	105.2	95.5	94.9	98.9	101.0
CH ₃ –C ₆ H ₅	102.0 ± 1.0	95.8	100.3	107.2	96.6	95.3	100.1	102.3
HC≡C–C ₆ H ₅	141.2 ± 1.4	136.8	140.7	148.4	137.7	134.9	140.8	142.3
CH ₂ =CH–C ₆ H ₅	115.2 ± 1.3	108.1	112.6	120.4	108.9	106.3	112.5	114.5
C ₂ H ₅ –C ₆ H ₅	100.2 ± 1.0	92.3	96.8	104.8	93.2	91.1	97.0	100.3
MD	-	-6.4	-2.1	+4.5	-5.7	-6.9	-2.2	+0.3
RMSE	-	6.7	2.8	4.9	6.0	7.1	2.9	1.4

^a Experimental values are obtained from ref 15. ^b For each method, the geometry optimization and single-point energy calculation are performed by using the same density functional as designated. The basis set for the geometry optimization is 6–31G(d), and the basis set for the single-point energy calculation is 6–311++G(2df,2p). ^c Unit: kcal/mol.

2. Performance of BMK in BDE Calculation

2.1. BMK Is Superior to the Other Functionals. Our finding initially arises from the study on the C–C BDEs, where we seek to systematically re-examine all the available experiment BDEs for carbon–carbon bonds by using theoretical methods. According to our previous work,⁹ although almost all of the DFT methods could not reliably calculate the absolute BDEs, some DFT methods could accurately predict the relative BDEs between analogous compounds. Thus we have tested a number of different functionals for calculating C–C BDEs of 12 representative compounds (Table 1). Not surprisingly, it is found that the popular B3LYP¹⁶ and B3P86¹⁷ methods systematically underestimate the C–C BDEs by 6.4 and 2.1 kcal/mol, respectively (as indicated by the mean deviations (MD) in Table 1). The root of mean square errors (RMSE) of the two methods are also as high as 6.7 and 2.8 kcal/mol.

Evidently the B3LYP and B3P86 functionals are not ideal for the BDE calculation. Consequently we turn to several newly developed functionals. These include the following: (1) KMLYP that uses a mix of Slater exchange and exact exchange for the exchange functional and a mix of the correlation functional of VWN and LYP;¹⁸ (2) X3LYP that is constructed for general-purpose applications in thermochemistry;¹⁹ (3) O3LYP that uses the OPTX exchange functional developed by Handy and Cohen;²⁰ (4) MPW1P86 that uses MPW1 for the exchange functional and the P86 nonlocal correction functional;²¹ and (5) BMK recently developed by Boese and Martin.²² Unfortunately it is found that except for BMK, all these new functionals fail to predict the C–C BDEs within chemical accuracy (~1 kcal/mol). The KMLYP functional overestimates the C–C BDEs by *ca.* 5 kcal/mol, whereas X3LYP, O3LYP, and MPW1P86 underestimate the C–C BDEs by *ca.* 2–7 kcal/mol.

Note that the BMK functional was developed to simulate a variable exact exchange by combining exact exchange (42%) and terms depending on the kinetic energy density.²² The purpose of this strategy was to generate a back-correction for excessive HF exchange in systems where that would be undesirable. Previously BMK has been shown to predict accurate heats of formation, reaction barriers, and enthalp-

ies.²² In a very recent study by Van Speybroeck and co-workers it was also reported that BMK could reliably predict the C–H BDEs with a mean deviation of *ca.* 0.5 kcal/mol.¹⁰ Here, our calculations of C–C BDEs show that BMK has a mean deviation of +0.3 kcal/mol and a root of mean square error of 1.4 kcal/mol. Thus we conclude that BMK is superior to the other functionals for BDE calculation.

2.2. Scope and Limitation of BMK in BDE Calculation.

The above work has shown that BMK can reliably predict C–C BDEs. Here we further examine whether or not BMK can accurately calculate the BDEs of other types of chemical bonds in organic molecules. To this end we systematically select a number of representative compounds that possess the C–H, C–C, C–F, C–Cl, O–H, O–O–, C–O, N–O, O–S, F–O, Cl–O, P–H, N–H, N–N, N–C, F–N, Cl–N, S–H, S–S, S–C, Si–H, Si–Si, Si–C, Si–O, Si–N, Si–F, and Si–Cl bonds (Table 2). The BDEs of these compounds are calculated by the BMK/6–311++G(2df,2p)//BMK/6–31G(d) method. For comparison we also show the predictions by the B3LYP/6–311++G(2df,2p)//B3LYP/6–31G(d) method.

Analysis of the calculation results indicates that both the B3LYP and BMK predictions exhibit good correlations with the experimental BDE values (Figure 1). However, it is evident from Figure 1 that the B3LYP method systematically underestimates the BDEs by *ca.* 5 kcal/mol (MD = -4.8 kcal/mol). The RMSE error of the B3LYP method is also as high as 5.7 kcal/mol. More seriously, from Table 2 we identify 22 compounds for which the B3LYP predictions differ from the corresponding experimental results by over 8 kcal/mol! The compounds possess chemical bonds including the C–Cl, O–O, C–O, S–O, C–N, N–N, S–S, Si–C, Si–O, Si–N, and Si–Cl bonds. The serious failure of the B3LYP method to calculate these particular bond energies casts more doubts on the reliability of using B3LYP to model organic chemistry.²³

In comparison to B3LYP, the BMK method dramatically improves the MD to -1.4 kcal/mol. The RMSE error of the BMK method is also significantly reduced to 2.7 kcal/mol. These parameters again indicate that BMK constitutes a good-quality, yet low-cost theoretical method for the predic-

Table 2. Comparison between the Experimental BDEs and Theoretical Predictions by the B3LYP, BMK, and G3//BMK Methods^a

compounds	exp	B3LYP ^b	BMK ^c	G3//BMK	G3	G3//B3LYP
CH ₃ –H	105.0 ± 0.1	102.9	104.4	104.6	104.2	104.3
H–C ₂ H ₅	100.5 ± 0.3	98.3	100.1	101.1	101.2	101.0
H–nC ₃ H ₇	100.9 ± 0.5	98.5	100.7	101.7	101.5	101.3
H–nC ₄ H ₉	100.7	98.5	100.3	101.3	101.5	101.3
H–iC ₄ H ₉	100.2 ± 1	98.8	100.8	101.8	101.8	101.6
H–sC ₄ H ₉	98.3 ± 0.5	94.9	97.2	98.9	99.2	98.9
H–tC ₄ H ₉	95.7 ± 0.7	91.9	95.0	97.2	97.4	97.2
HC≡C–H	133.3 ± 0.1	133.6	135.0	133.5	132.9	132.2
H–CHCH ₂	111.2 ± 0.8	108.3	109.7	110.3	110.3	110.1
H–CH ₂ CHCH ₂	88.2 ± 0.7	83.8	86.1	87.4	86.9	87.4
H–CH(CH ₃)CHCH ₂	83.8	79.7	82.6	84.7	84.2	84.6
H–CH ₂ CHCHCH ₃ (<i>trans</i>)	85.3	83.1	85.5	87.2	86.8	87.2
H–CH ₂ CHCHCHCH ₂	83 ± 3	77.7	80.2	82.4	81.5	82.4
H–CH(C ₂ H ₅) ₂	76.6 ± 1.0	72.1	74.9	77.8	77.1	78.2
H–CH(CH ₃)CCCH ₃	87.3 ± 2.3	82.8	86.3	88.6	88.6	88.4
H–cyclopropylmethyl	97.4 ± 1.6	95.3	97.3	98.7	98.6	98.6
H–cyclopenta-1,3-dien-5-yl	83.9 ± 0.5	79.4	81.3	82.8	83.4	82.6
H–cyclopentyl	95.6	92.5	94.9	96.5	96.3	96.2
H–cyclohexa-1,4-dien-3-yl	76.0 ± 1.2	70.7	73.7	76.4	75.7	76.3
H–cyclohexyl	99.5	95.1	97.7	99.2	99.5	99.2
C ₆ H ₅ –H	112.9 ± 0.5	110.5	111.7	114.7	114.6	114.3
H–CN	126.3 ± 0.2	128.2	131.2	126.5	127.5	126.4
H–CH ₂ CN	96	92.3	95.3	96.2	96.1	96.2
H–CH(CH ₃)CN	94.0 ± 3	87.2	90.7	92.6	92.8	92.6
H–C(CH ₃) ₂ CN	91.9	(83.5)	87.5	89.9	90.3	89.8
H–CHCO	107.1	103.4	106.3	105.8	105.5	105.7
H–COCHCH ₂	89.1	88.3	88.7	90.2	91.2	90.1
H–COC ₂ H ₅	88.7	87.0	87.2	89.7	89.6	89.7
H–CH ₂ CHO	94.3 ± 2.2	91.8	94.2	95.2	95.4	95.2
H–CH ₂ COCH ₃	95.9 ± 0.7	93.0	95.4	96	96.3	95.9
H–CH(CH ₃)COCH ₃	92.3 ± 1.7	86.7	89.6	91.2	91.6	91.4
H–CH ₂ OCH ₃	96.1	93.3	94.7	96.5	96.4	96.4
H–tetrahydrofuran-2-yl	92.1 ± 1.6	89.9	91.6	93.7	93.8	93.7
H–CH ₂ OH	96.1 ± 0.15	93.6	94.8	96.4	96.3	96.3
H–CH(OH)CHCH ₂	81.6 ± 1.8	77.6	79.7	82.8	80.1	80.8
H–CH ₂ F	101.3 ± 1	98.7	100.1	101.2	101.3	101.1
H–CHF ₂	103.2 ± 1	100.3	101.8	103.7	101.8	101.8
H–CHFCl	100.8 ± 2.4	96.0	98.2	99.4	99.2	99.2
H–CF ₂ Cl	100.7 ± 2	98.4	100.4	102.4	102.1	102.2
H–CFCl ₂	98.2 ± 2	94.2	96.6	98.4	97.9	98.0
H–CH(CH ₃)Cl	97.2 ± 0.4	94.3	96.9	98.1	97.8	97.6
H–C(CH ₃)Cl ₂	95.1 ± 1.2	91.5	94.5	95.9	95.4	95.4
H–C ₂ F ₅	102.7 ± 0.5	99.7	102	104.3	104.2	104.2
H–CCl ₂ CHCl ₂	94 ± 2	88.9	93.2	94.8	94.5	94.6
H–CH ₂ SCH ₃	93.7 ± 1.4	91.1	94.0	94.5	94.0	94.0
H–CF ₃	106.4 ± 0.7	103.3	105.2	108.3	107.0	107.1
H–COCF ₃	91 ± 2	90.1	90.7	93.2	93.0	93.1
H–CHO	88.0 ± 0.2	86.1	86.3	88.5	88.4	88.4
H–CH ₂ OH	96.1 ± 0.2	93.4	94.7	96.4	96.3	96.3
H–CH ₂ SH	93.9 ± 2.0	92.6	95.3	95.6	95.2	95.2
CH ₃ –CH ₃	90.2 ± 0.2	84.2	90.2	88.8	88.4	88.7
CH ₃ –C≡CH	126.5 ± 1.0	124.1	129.7	126.0	125.3	124.7
CH ₃ –CH ₂ CCH	76.6 ± 1.2	69.5	77.4	77.9	77.7	77.9
CH ₃ –CH ₂ C(CH ₃)CH ₂	74.1 ± 1.0	67.3	75.5	76	75	75.7
CH ₃ –CH(CH ₃)CCCH ₃	76.7 ± 1.5	(66.1)	75.3	77.5	77.2	77.2
nC ₃ H ₇ –CH ₂ CHCH ₂	75.0 ± 1.0	(63.4)	72.2	74.5	73.9	74.4
CH ₃ –CH ₂ CN	83.2 ± 3	(74.6)	82.8	82.9	82.5	82.9
CH ₃ –CH ₂ OH	87.2 ± 1.0	79.8	86.1	86.8	86.3	86.5
CN–CN	136.7 ± 1.6	142.1	147.5	138.1	139.8	137.8
CH ₃ –CH ₂ SH	82.5 ± 2.2	75.9	83.9	83.6	82.7	82.9
F–CF ₃	130.7 ± 0.5	123.3	128.7	131.8	130.6	130.3
F–CF ₂ Cl	122.3	116.4	121.5	123.9	123.6	123.5
F–CH ₃	110.0 ± 2.0	107.7	111.3	109.9	109.7	109.8
Cl–CN	101.0 ± 2.0	102.2	107.7	102.3	103.8	102.4
Cl–CF ₃	87.3 ± 0.9	79.9	86.5	88.1	87.4	87.0
Cl–CHFCl	82.7 ± 3.2	(74.0)	81.3	81.3	81.3	80.9
Cl–CFCl ₂	76.7 ± 2	(67.2)	75.0	77.1	76.9	76.6
Cl–CH ₃	83.7 ± 0.4	79.2	86.0	82.5	82.5	82.4
HO–H	118.8 ± 0.1	115.6	116.4	118.1	118.0	118.1
CH ₃ O–H	104.6 ± 0.7	99.6	101.1	105.0	105.1	104.8

Table 2. Continued

compounds	exp	B3LYP ^b	BMK ^c	G3//BMK	G3	G3//B3LYP
CF ₃ O–H	118.8	114.8	117.2	119.3	119.2	119.2
H–OC(CH ₃) ₃	106.3 ± 0.7	101.1	102.3	106.8	106.8	106.7
H–OOH	87.8 ± 0.5	82.6	83.4	87.1	86.7	87.1
H–ONO	78.3 ± 0.5	74.1	77.7	77.8	77.6	78.0
HO–OH	50.4 ± 0.1	46.1	47.3	48.6	48.2	48.7
HO–OCH ₂ C(CH ₃) ₃	46.3 ± 1.9	(35.4)	41.4	46.4	42.8	42.5
HO–OF	45.6 ± 2	42.7	42.9	45.2	44.8	45.4
HO–OCH ₃	44.7 ± 1	37.5	39.5	43.6	43.4	43.4
CH ₃ O–OCH ₃	39.0 ± 1.5	(28.5)	31.4	38.7	39.0	38.4
HO–CH ₃	92.0 ± 0.2	87.1	92.1	91.0	90.5	90.9
CH ₃ –OCH ₃	83.6 ± 1.0	(75.4)	81.7	83.6	83.3	83.2
CH ₃ –OC(O)H	91.7 ± 3	(82.6)	90.4	91.7	92.8	90.5
CH ₃ –ONO	58.6	51.7	60.1	58.2	57.8	58.5
HO–NO	49.3	46.5	47.2	48.3	47.6	48.5
CH ₃ O–NO	41.8 ± 1.0	36.7	38.6	42.7	42.4	42.8
nC ₃ H ₇ O–NO	42.8 ± 1.5	35.8	37.9	42.6	42.2	42.6
iC ₃ H ₇ O–NO	41.9 ± 1	35.8	37.8	43	42.9	43.1
nC ₄ H ₉ O–NO	42.5 ± 1.5	35.9	37.6	42.4	42.3	42.8
iC ₄ H ₉ O–NO	42.0 ± 1.5	35.6	37.4	42.4	42.2	42.6
sC ₄ H ₉ O–NO	41.5 ± 0.8	36.1	37.6	42.9	46.3	43.1
HO–NO ₂	48.8	45.3	48.8	48.5	48.2	48.7
HO ₂ –NO ₂	23.9 ± 0.7	18.4	20.3	23.9	23.6	24.2
HO–SH	70.1 ± 4	64.9	69.2	68.9	68.2	68.4
HO–SCH ₃	72.6 ± 3	65.7	71.2	72.1	70.7	70.5
HO–SOH	74.9 ± 3	(66.6)	71.0	72.2	71.7	71.6
F–OCF ₃	48 ± 1	41.5	41.3	45.6	45.7	45.6
Cl–OCH ₃	47.5	41.8	45.8	48.5	48.7	47.9
HO–Cl	55.8	52.1	55.0	54.8	54.8	54.6
H–PH ₂	83.9 ± 0.5	80.6	81.5	81.5	81.6	81.7
H–NH ₂	107.6 ± 0.1	104.7	106.2	106.8	106.8	106.7
H–NHCH ₃	101.6 ± 2	96.2	97.8	99.7	99.6	99.4
H–N(CH ₃) ₂	94.6 ± 2	89.8	91.7	94.2	94.2	93.9
H–NF ₂	75.7 ± 2.5	71.3	72.7	74.2	73.8	74.3
H–NO	47.7	46.8	46.1	48.2	47.5	48.4
H ₂ N–NH ₂	65.5 ± 0.4	60.8	65.8	64.5	64.1	64.3
NH ₂ –NHCH ₃	65.9 ± 2	(57.9)	63.4	64	63.6	63.7
NH ₂ –N(CH ₃) ₂	62.1 ± 2	(53.9)	60.1	62.5	62.3	62.1
F ₂ N–NF ₂	21 ± 1	(11.6)	17.3	20.7	19.6	20.8
CH ₃ –NO	41.1	36.1	39.8	39.1	38.0	39.0
tC ₄ H ₉ –NO	39.9	(31.4)	38.6	41.6	41.0	41.6
CH ₃ –NO ₂	62.3 ± 0.5	54.8	61.5	60.5	59.9	60.3
CH ₃ –N ₂ CH ₃	52.5	47.4	53.6	53.7	53.1	53.5
F–NO	56.2	60.7	57.3	61.2	61.7	61.7
F–NO ₂	52.9	54.1	52.4	54.8	55.3	55.2
F–NH ₂	68.5	67.9	68.9	69.3	69.2	69.3
Cl–NO	38.0 ± 0.2	37.9	36.8	37.7	37.4	37.5
Cl–NO ₂	33.9 ± 0.3	32.8	34.7	34.7	34.6	34.2
HS–H	91.2 ± 0.1	89.0	89.4	90.4	90.3	90.4
H–SCH ₃	87.4 ± 0.5	83.8	85.7	87.3	86.2	86.0
H–SOH	79 ± 3.5	75.0	75.4	77.5	77.2	77.3
PhS–H	83.5 ± 1.1	76.7	77.8	81.2	80.8	81.2
CH ₃ S–SCH ₃	65.2 ± 0.9	(55.4)	65.1	64.7	63.1	62.2
HS–CH ₃	74.7 ± 1	68.7	75.0	73.2	72.8	72.9
HS–C(O)H	74 ± 2	68.8	72.5	72.7	72.9	72.7
CH ₃ S–CH ₃	73.6 ± 0.8	65.7	73.6	73.2	71.9	71.8
SiH ₃ –H	91.7 ± 0.5	90.0	91.6	92.1	91.7	91.6
H–SiH ₂ CH ₃	92.7 ± 1.2	90.5	91.5	92.2	92.7	92.6
H–SiH(CH ₃) ₂	93.5 ± 1.2	91.3	93.0	93.9	93.7	93.6
H–Si ₂ H ₅	89.1 ± 2	87.1	87.7	88.4	88.9	88.8
Me ₃ Si–H	94.6 ± 1.7	91.9	93.3	94.3	94.6	94.5
SiF ₃ –H	103.2 ± 1.2	97.4	99.8	100.7	101.0	101.1
SiH ₃ –SiH ₃	76.7 ± 1	70.4	75.5	76.0	76.0	75.9
SiH ₃ –CH ₃	89.6 ± 1.2	82.1	89.6	87.8	87.6	87.6
Me ₃ Si–CH ₃	94.2 ± 2	(84.3)	92.3	93.0	92.5	92.4
Me ₃ Si–OH	132.6 ± 2.0	(122.8)	129.1	131.9	131.8	131.7
Me ₃ Si–OMe	122.6 ± 2.6	(106.4)	113.9	120.5	120.6	119.9
Me ₃ Si–NMe ₂	97.5 ± 2	(82.4)	91.7	98.0	98.2	97.6
SiH ₃ –F	152.5 ± 1.2	(144.5)	148.5	150.8	150.7	150.3
Me ₃ Si–F	159.9 ± 4.8	154.0	158.2	161.5	161.6	161.2
SiH ₃ –Cl	109.5 ± 1.7	103.2	111.9	108.2	108.4	107.9
SiCl ₃ –Cl	111.3 ± 1	(100.1)	110.6	110.7	110.9	110.5
MD		–4.8	–1.4	–0.004	–0.2	–0.3
RMSE		5.7	2.7	1.2	1.5	1.4

^a Unit: kcal/mol. For the B3LYP and BMK methods, the basis set for the geometry optimization is 6–31G(d), and the basis set for the single-point energy calculation is 6–311++G(2df,2p). ^b Values in bold and in parentheses are theoretical predictions that differ from the corresponding experimental BDEs by more than 8 kcal/mol. ^c Values in bold with underlines are theoretical predictions that differ from the corresponding experimental BDEs by more than 5 kcal/mol.

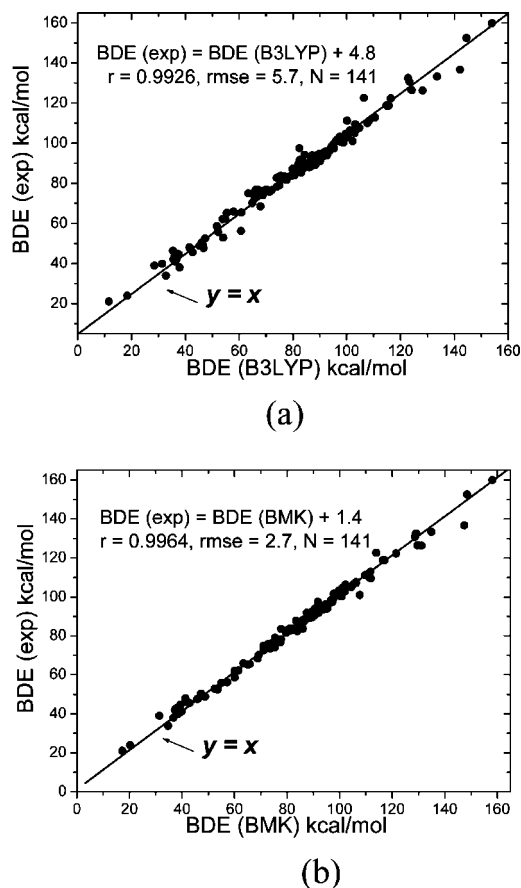


Figure 1. Correlation of the experimental BDE values with the B3LYP (a) and BMK (b) predictions.

tion of BDEs for most types of chemical bonds commonly found in organic molecules. Therefore, if a DFT method *has to* be used to estimate the strength of a chemical bond of an organic compound (either because of the limitation of CPU resource or due to the bulkiness of the molecule), we suggest that BMK be considered with priority.

Nonetheless, it should also be pointed out that BMK, like all the other DFTs tested previously, is *NOT* free from failure in predicting BDEs. As shown in Table 2, the BMK predictions for eight compounds are different from the corresponding experimental values by over 5 kcal/mol. These compounds include NC-CN (error = 10.8 kcal/mol), Cl-CN (error = 6.7 kcal/mol), HO-OCH₃ (error = 5.2 kcal/mol), CH₃O-OCH₃ (error = 7.6 kcal/mol), F-OCF₃ (error = 6.7 kcal/mol), PhS-H (error = 5.7 kcal/mol), Me₃Si-OMe (error = 8.7 kcal/mol), and Me₃Si-NMe₂ (error = 5.8 kcal/mol). Evidently these magnitudes of errors are not acceptable for any meaningful theoretical prediction.

Note that the failure of the BMK method in predicting the above eight BDEs is not due to the limited size of the basis set. As demonstrated in Table 3, BMK still erratically predicts the BDE values of the same eight compounds even when the basis set is extrapolated to the infinite size using the following empirical function as developed by Kahn and Bruice.²⁴

$$E_x = E_\infty + A_3 X^{-3} + A_5 X^{-5} \quad (1)$$

The similar extrapolations to infinite basis set based on DFT calculations to O-H and O-O BDEs were reported.^{25,26}

This finding prompts us to develop the G3//BMK method, which hopefully may combine the strengths of both the composite *ab initio* approach (strength in handling thermodynamics as compared to the other *ab initio* approaches) and the BMK method (strength in handling organic radicals as compared to the other DFT methods).

3. Development of G3//BMK Theory

3.1. Scale Factor for BMK. As demonstrated in several previous studies, the use of harmonic frequency scaling factors may improve the accuracy in the calculation of enthalpies.^{27,28} For the purpose of developing a high-quality G3//BMK theory, we need to obtain the scale factor for the BMK method (specifically, BMK/6-31G(d)) at first.

To save computing time we select 28 molecules from the G2/97 test set,²⁹ for which 169 experimental harmonic frequencies are available with high precision (Supporting Information). The BMK/6-31G(d) method is used to calculate these frequencies. Subsequently we determine the optimum scaling factor λ through a least-squares procedure by minimizing the residuals

$$\Delta = \sum_i (\lambda \omega_i^{\text{theor}} - \tilde{\nu}_i^{\text{exp}})^2 \quad (2)$$

leading to

$$\lambda = \frac{\sum_i \omega_i^{\text{theor}} \tilde{\nu}_i^{\text{exp}}}{\sum_i (\omega_i^{\text{theor}})^2} \quad (3)$$

where ω_i^{theor} and $\tilde{\nu}_i^{\text{exp}}$ are the i th theoretical harmonic and i th experimental fundamental frequencies (in cm⁻¹), respectively. Using this approach the optimum scaling factor λ is determined to be 0.9414 for the BMK/6-31G(d) method.

3.2. G3//BMK Protocol. The steps in G3 theory have been discussed in detail in ref 30. In the BMK-based method proposed here, we have made two modifications. First, the geometries are obtained at the BMK/6-31G(d) level instead of MP2(FU)/6-31G(d) (Note: FU = all electrons included in the correlation calculation). Second, the zero-point energies are obtained at the BMK/6-31G(d) level (At the same time, we also calculated the B3LYP/6-31G(d) scale factor using these 28 molecules, and the result is 0.9615, which is nearly the same with Radom's result 0.9614.²⁷ Considering that in G3//B3LYP theory the B3LYP/6-31G(d) scale factor 0.96 is used, so we used 0.94 in G3//BMK.) instead of HF/6-31G(d). All of the other steps remain the same with the exception of the values of the higher-level correction parameters (see below). The G3 theory modified in this manner are referred to as G3//BMK theory (Table 4).

The higher-level correction (HLC) takes into account remaining deficiencies in the energy calculations and is similar to that used in G3 theory except that the parameters have been reoptimized. The HLC is $-An_\beta B(n_\alpha n_\beta)$ for molecules and $-Cn_\beta D(n_\alpha n_\beta)$ for atoms (including atomic ions). The n_β and n_α are the number of β and α valence electrons, respectively, with $n_\alpha \geq n_\beta$. The A , B , C , and D values are chosen to give the smallest average absolute deviation for the G2/97 test set of experimental energies. Note that the G2/97 test set contains 148 enthalpies of

Table 3. Effect of Basis Sets on BMK Calculation^{a,c}

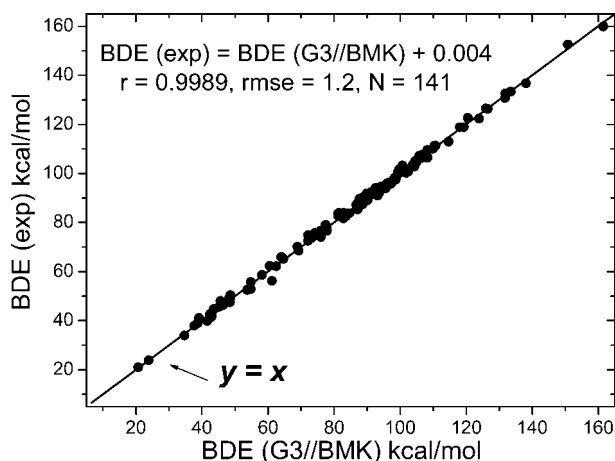
compounds	exp	6-311++G (2df,2p)	cc-pVDZ	cc-pVTZ	cc-pVQZ	∞^b
CN-CN	136.7 ± 1.6	147.5	146.7	146.9	146.7	146.5
Cl-CN	101.0 ± 2.0	107.7	102.6	105.9	106.6	107.1
HO-OCH ₃	44.7 ± 1	39.5	41.9	40.8	39.9	39.0
CH ₃ O-OCH ₃	39.0 ± 1.5	31.4	33.9	32.8	31.8	30.8
F-OCF ₃	48 ± 1	41.3	40.5	42.1	41.8	41.3
PhS-H	83.5 ± 1.1	77.8	75.2	77.3	78.1	78.8
Me ₃ Si-OMe	122.6 ± 2.6	113.9	108.6	114.0	114.5	114.6
Me ₃ Si-NMe ₂	97.5 ± 2	91.7	88.3	91.7	91.9	91.8

^a The basis set for the geometry optimization is 6-31G(d). ^b Extrapolated values to infinite basis set. ^c Unit: kcal/mol.

Table 4. Steps in G3//BMK Theory^a

step	G3//BMK
geometry	BMK/6-31G(d)
single-point energies	MP4(FC)/6-31G(d) MP4(FC)/6-31+G(d) MP4(FC)/6-31G(2df,p) QCISD(T,FC)/6-31G(d) MP2(FU)/G3large
spin-orbit correction (Δ SO)	atomic species
high-level correction (Δ HLC)	molecules ($A = 6.652$, $B = 3.039$) atoms ($C = 6.589$, $D = 1.281$)
zero-point energy (ZPE)	BMK/6-31G(d)

^a Note: FC = frozen core approximation for the correlation calculation.

**Figure 2.** Correlation of the experimental BDE values with G3//BMK predictions.

formation of neutrals at 298 K ($\Delta_f H^0$), 88 ionization potentials (IP_0), 58 electron affinities (EA_0), and 8 proton affinities (PA_0) for a total of 302 reaction energies.²⁹ In our assessment, we have used the G2/97 test set less three ionization potentials ($C_6H_5CH_3 \rightarrow C_6H_5CH_3^+$, $C_6H_5NH_2 \rightarrow C_6H_5NH_2^+$, $C_6H_5OH \rightarrow C_6H_5OH^+$) resulting in a total of 299 energies. These energies are calculated by the following equations:

$$\begin{aligned} \Delta_f H^0(A_x B_y H_z, 298 \text{ K}) &= \Delta_f H^0(A_x B_y H_z, 0 \text{ K}) + \\ &[H^0(A_x B_y H_z, 298 \text{ K}) - H^0(A_x B_y H_z, 0 \text{ K})] - \\ &x[H^0(A, 298 \text{ K}) - H^0(A, 0 \text{ K})]_{\text{st}} - \\ &y[H^0(B, 298 \text{ K}) - H^0(B, 0 \text{ K})]_{\text{st}} - \\ &z[H^0(H, 298 \text{ K}) - H^0(H, 0 \text{ K})]_{\text{st}} \quad (4) \end{aligned}$$

where $\Delta_f H^0(A_x B_y H_z, 0 \text{ K}) = x\Delta_f H^0(A, 0 \text{ K}) + y\Delta_f H^0(B, 0 \text{ K}) + z\Delta_f H^0(H, 0 \text{ K}) - \Sigma D_0$

$$EA_0 = E_0(\text{neutral}) - E_0(\text{anion}) \quad (5)$$

$$IP_0 = E^0(\text{cation}) - E^0(\text{neutral}) \quad (6)$$

and

$$PA_0 = E^0(\text{neutral}) - E^0(\text{cation}) \quad (7)$$

For G3//BMK theory, our calculations suggest that $A = 6.652$ mhartrees, $B = 3.039$ mhartrees, $C = 6.589$ mhartrees, and $D = 1.281$ mhartrees. Thus the final G3//BMK energy can now be calculated by the following equation

$$E_0(\text{G3//BMK}) = E[\text{MP4(FC)/6-31G(d)}] + \Delta(+)+\Delta(2\text{df,p})+\Delta(\text{QCI})+\Delta+\Delta\text{SO}+\Delta\text{HLC}+\text{ZPE} \quad (8)$$

where

$$\begin{aligned} \Delta(+) &= E[\text{MP4(FC)/6-31+G(d)}] - E[\text{MP4(FC)/6-31G(d)}] \\ \Delta(2\text{df,p}) &= E[\text{MP4(FC)/6-31G(2df,p)}] - E[\text{MP4(FC)/6-31G(d)}] \\ \Delta(\text{QCI}) &= E[\text{QCISD(T,FC)/6-31G(d)}] - E[\text{MP4(FC)/6-31G(d)}] \\ \Delta &= E[\text{MP2(FU)/G3large}] - E[\text{MP2(FC)/6-31G(2df,p)}] \\ &\quad - E[\text{MP2(FC)/6-31+G(d)}] + E[\text{MP2(FC)/6-31G(d)}] \quad (9) \end{aligned}$$

4. BDEs Predicted by G3//BMK

To test the performance of the G3//BMK method, we use it to recalculate the 141 BDE values of the diverse types of chemical bonds as listed in Table 2. It is found that the G3//BMK predictions are in excellent agreement with all the experimental data (Figure 2). The correlation coefficient is as high as 0.9989, and the mean deviation is as low as -0.004 kcal/mol. Remarkably the RMSE error of the G3//BMK predictions is only 1.2 kcal/mol, which is comparable to the error bar of most of the experimental values (*ca.* 1–3 kcal/mol). Furthermore, there is only one compound (namely, F-NO) for which the G3//BMK prediction (61.2 kcal/mol) disagrees with the corresponding experimental value (56.2 kcal/mol) by over 3 kcal/mol.

In comparison with the G3//BMK method, the standard G3 method exhibits a worse performance in predicting the BDEs. As shown in Table 2, the mean deviation and the RMSE error of the G3 method are -0.2 and 1.5 kcal/mol, respectively. More importantly, there are six compounds (namely, CN-CN, HO-SOH, CH_3 -NO, $HO-OCH_2C(CH_3)_3$, sC_4H_9O -NO, and F-NO) for which the G3 predictions (139.8, 71.7, 38.0, 42.8, 46.3, and 61.7 kcal/mol) disagree with the

corresponding experimental values (136.7, 74.9, 41.1, 46.3, 41.5, and 56.2 kcal/mol) by over 3 kcal/mol. The relatively poor performance of the G3 method was previously attributed to the deficiency of the MP2 theory in the geometry optimization for organic radicals.³¹

To improve the performance of the G3 method Baboul et al. once proposed the G3//B3LYP theory where the geometries and zero-point energies are obtained from the B3LYP method.³¹ Here our calculations show that the G3//B3LYP predictions of the BDEs have a mean deviation of -0.3 kcal/mol and a RMSE error of 1.4 kcal/mol. These quantities indicate that G3//BMK is also superior to G3//B3LYP in handling BDEs. In agreement with this argument, four compounds (HO-OCH₂C(CH₃)₃, HO-SOH, F-NO, and CH₃S-SCH₃) are found in Table 2 for which the G3//B3LYP predictions (42.5, 71.6, 61.7, and 62.2 kcal/mol) differ from the corresponding experimental values (46.3, 74.9, 56.2, and 65.2 kcal/mol) by over 3 kcal/mol.

It should be noted, the difference between G3//BMK and G3//B3LYP is the use of BMK versus B3LYP for the geometries (and harmonic frequencies). We selected HO-OCH₂C(CH₃)₃ and CH₃S-SCH₃ from Table 2 for example, which of whose BDEs by G3//BMK disagrees with G3//B3LYP by over 2 kcal/mol to make a comment on the geometries from B3LYP versus BMK. We compared geometries of these two compounds and the corresponding radicals using BMK/6-31G(d) and B3LYP/6-31G(d), respectively, and the bond lengths, the bond angles, and the dihedral angles were shown in the Supporting Information.

From these data, we can make a conclusion that there are large differences between BMK and B3LYP geometries for molecules and radicals as well. Note that, in OCH₂C(CH₃)₃ radical, the O-C-C angle is about 8° difference between BMK and B3LYP.

It also should be noted that the modification for different purposes based on Gaussian-*n* theory and its development³² with the use of new test set³³ is still promising.

5. Conclusions

The ability to reliably and efficiently calculate the bond dissociation enthalpies of various organic molecules is valuable to a number of subdisciplines of chemistry. In the present study we report our findings on the basis of systematic examinations that the BMK functional significantly outperforms the other popular density functional theory methods including B3LYP, B3P86, KMLYP, MPW1P86, O3LYP, and X3LYP for the BDE calculation.

However, it is also found that even the BMK functional may dramatically fail in predicting the BDEs of some chemical bonds. To solve this problem, we develop a new composite *ab initio* method named G3//BMK by combining the strengths of both the G3 theory and BMK. G3//BMK is found to outperform the G3 and G3//B3LYP methods. It can accurately predict the BDEs of diverse types of chemical bonds in various organic molecules within a precision of *ca.* 1.2 kcal/mol.

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Supporting Information Available: 169 vibrational frequencies used for the optimization of the scale factor, 299 energies used for the optimization of A, B, C, and D, and the geometry comparison of two compounds and corresponding radicals of BMK/6-31G(d) and B3LYP/6-31G(d). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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