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Theoretical Study for the Potential Energy Surface of BH_5 Using the Multicoefficient Correlated Quantum Mechanical Methods

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The structures and energies of BH_5 and the transition state for the hydrogen scrambling have been studied using recently developed multicoefficient correlated quantum mechanical methods (MCCMs). We have obtained the dissociation energies between 5.76 and 6.15 kcal/mol, and the barrier heights between 5.44 and 5.83 kcal/mol, which agree very well with the previous results at the CCSD(T)/TZ(3d1f1g,2p1d) level. We have also calculated the potential energy curves for the dissociation of BH_5 to BH_3 and H_2. The lower levels of theory were unable to plot correct potential curves, whereas the MCCM methods give very good potential energy curves and requires much less computing resources than the CCSD(T)/TZ(3d1f1g,2p1d) level.

1. Introduction

Weak chemical interactions play a central role in chemistry and biology. They are responsible for polymer properties, tertiary structure in macromolecules, molecular fluid and molecular solid properties, conformational structures and preferences of molecules, and energy transfer between molecules and between molecular moieties, and, in a broad sense, they are even responsible for chemical reactions. Empirical and semiempirical potential energy functions (e.g., Lennard-Jones−Coulomb, exponential-six, and others) have long been quite successful at predicting and modeling weak chemical interactions between molecules and between molecular moieties.[1]

In principle, it is known how to compute the thermochemical properties of most molecules to very high accuracy using quantum chemical calculations. This can be achieved by using very high levels of correlation methods, such as coupled cluster or quadratic configuration methods, and very large basis sets containing high angular momentum functions, and the results of these calculations can be extrapolated to the complete basis set limit. However, it is still almost impractical except for small systems.[2,3] An alternative approach applicable for larger molecules is to use a series of high level correlation calculations [e.g., QCISD(T), MP4, CCSD(T)] with moderate sized basis sets to approximate the result of a more expensive calculation. The Gaussian-*n* series use this idea to calculate thermochemical data.[3−9] In the G2 theory, the energy is estimated using corrections that refer to the MP4/6-311+(3df,2p) level of theory, and the remaining correlation effect and the basis-set deficiency are corrected by adding the higher-level correction (HLC). In the G3 method, the HLC term involves different constants for atoms than for molecules, and thus, it cannot be used to predict continuous potential energy surfaces along bond breaking coordinates.[10] Allen and co-workers have performed the dual extrapolation of relative energy predictions to the one- and *n*-particle ab intio limits within the focal-point scheme.[11−16] The focal-point scheme includes the following: (a) use of a family of basis sets which systematically approaches completeness (e.g., the cc-pV*XZ*, aug-cc-pV*XZ*, and cc-pCV*XZ* sets); (b) application of low levels of theory with prodigious basis sets (typically direct RHF and MP2 computations with several hundred basis functions); (c) higher order valence correlation treatments [CCSDT, CCSD(T), BD(TQ), MP4, and MP5] with the largest possible basis sets; (d) layout of a two-dimensional extrapolation grid based on an assumed additivity of correlation *increments* to the energy difference of concern; and (e) eschewal of empirical corrections.[13] Another approach for calculating thermochemical data that has been proposed is a scaling of the calculated energy using multiple parameters determined by fitting to experimental data. Recently, Truhlar and co-workers have suggested more elaborate schemes that combine scaling, extrapolation to infinite basis set, and fitting to a set of experimental data.[10,17−22] In these methods, the total energy is written as a linear combination of energy terms with different basis sets, and coefficients are adjusted to fit experimental data (atomization energies). The correction of the basis-set deficiency is included in some of the coefficients. These linear combination methods were called multicoefficient correlated quantum mechanical methods (MCCMs). The MCCM methods have been applied successfully to reproduce proton affinities of molecules,[23] structures, and energies for hydrogen bonded complexes[24] and protonated water clusters,[25] although no such experimental results are included in developing the MCCM parameters. The MCCM methods can also be used to calculate the potential energy surface for bond dissociation because it does not have the HLC term.[10]

In this study, we have performed the MCCM calculations for the potential energy surface of BH_5. BH_5 was suggested as an intermediate of the acidolysis of BH_4^- in aqueous solution, eq 1:[26]

$$H^+ + BH_4^- + 3H_2O \rightarrow 4H_2 + B(OH)_3 \qquad (1)$$

Kinetic study suggests that BH_5 is formed by reaction of BH_4^- with either H^+ or H_2O followed either by loss of H_2 or by reaction of BH_5 with OH^- to regenerate BH_4^-. In basic D_2O,

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unreacted BH_4^- turned into, first, BH_3D^-, then $BH_2D_2^-$, etc.[27] BH_5 has been detected spectroscopically in a low-temperature matrix.[28] Schreiner et al. have performed extensive calculations for the BH_5 systems.[29] They found that geometry and energy of BH_5 depend very much on the level of theory and the size of basis sets. The HF level of theory is inadequate for BH_5, and even CCSD(T) level with the DZP basis sets cannot predict the structure of BH_5 correctly. BH_5 should be considered as a molecule with chemical bonds between BH_3 and H_2.[29] This is a weak 2-electron−3-center bond, and the correct description for the bond dissociation can be a critical test for theory. We have also calculated the transition state for the hydrogen scrambling in BH_5. Four MCCM calculations, namely, MCCM-UT-MP4SDQ, MCCM-UT-CCSD, MC-QCISD, and MCG3 have been performed along with the G3 and CCSD(T)/cc-pVQZ calculations for comparison.

2. Computational Methods

All electronic structure calculations were performed with the *Gaussian 98* program[30] packages. Initial geometries for BH_5 complex were fully optimized at the QCISD and CCD levels of theory with the TZ2P basis sets, and then the structures of the BH_5 complex were partially optimized by fixing the distance between Boron and the center of H_2 along the dissociation coordinate of BH_5 to BH_3 and H_2. The MCCM potential energy curves were calculated using these partially optimized structures. The full geometry optimization was also performed, and frequencies and zero-point energies for H_2, BH_3, and BH_5 were obtained using the optimized structures. The structures optimized at the QCISD/TZ2P level have been used for the potential energy curve at the G3 level. Although we followed the G3 procedures, it is not the real G3, because the G3 level uses the MP2/6-31G(d) method for the geometry optimization. Therefore, we will denote it as G3//QCISD/TZ2P. For the potential energy curve for BH_5 dissociation, the single-point MCCM calculations were performed using the structures partially optimized at the QCISD/TZ2P level. So these calculations are denoted as MCCM//QCISD/TZ2P.

All of the multicoefficient correlated quantum mechanical methods have been described elsewhere in detail;[10,17,19−21] therefore, only a short description of each method employed will be given here. Because all of these methods involve differences between energies at different basis sets and theory levels, a short notation has been used in order to write the equation for a multilevel energy succinctly. In this notation, the pipe ‘‘|” is used to represent the energy difference either between two one-electron basis sets B1 and B2 or between two levels of electronic structure theory L1 and L2, e.g., Møller−Plesset second-order perturbation theory and Hartree−Fock theory. The energy difference between two basis sets is represented as

$$\Delta E(\mathrm{L/B2|B1}) = E(\mathrm{L/B2}) - E(\mathrm{L/B1}) \tag{2}$$

where L is a particular electronic structure method, and B1 is smaller than B2. The energy change that occurs upon improving the treatment of the correlation energy is represented by

$$\Delta E(\mathrm{L2|L1/B}) = E(\mathrm{L2/B}) - E(\mathrm{L1/B}) \tag{3}$$

where L1 is a lower level of theory than L2 and B is a common one-electron basis set. Finally, the change in energy increment due to increasing the level of the treatment of the correlation energy with one basis set as compared to the increment obtained with a smaller basis set is represented as

$$\Delta E(\mathrm{L2|L1/B2|B1}) = E(\mathrm{L2/B2}) - E(\mathrm{L1/B2}) - [E(\mathrm{L2/B1}) - E(\mathrm{L1/B1})] \tag{4}$$

The Utah variant of MCCM (MCCM-UT-L) methods are written as

$$E(\mathrm{MCCM\text{-}UT\text{-}L}) = c_1E(\mathrm{HF/cc\text{-}pVDZ}) + c_2\Delta E(\mathrm{HF/cc\text{-}pVTZ|cc\text{-}pVDZ}) + c_3\Delta E(\mathrm{MP2|HF/cc\text{-}pVDZ}) + c_4\Delta E(\mathrm{MP2|HF/cc\text{-}pVTZ|cc\text{-}pVDZ}) + c_5\Delta E(\mathrm{L|MP2/cc\text{-}pVDZ}) + E_{\mathrm{SO}} + E_{\mathrm{CC}} \tag{5}$$

where L is either MP4SDQ or CCSD. Equations for the electronic energies for the multicoefficient Gaussian-3 (MCG3)[10] and the multicoefficient QCISD (MC-QCISD)[20] methods are given below:

$$E(\mathrm{MCG3}) = c_1E(\mathrm{HF/6\text{-}31G(}d\mathrm{)}) + c_2\Delta E(\mathrm{HF/MG3|6\text{-}31G(}d\mathrm{)}) + c_3\Delta E(\mathrm{MP2|HF/6\text{-}31G(}d\mathrm{)}) + c_4\Delta E(\mathrm{MP2|HF/MG3|6\text{-}31G(}d\mathrm{)}) + c_5\Delta E(\mathrm{MP4SDQ|MP2/6\text{-}31G(}d\mathrm{)}) + c_6\Delta E(\mathrm{MP4SDQ|MP2/6\text{-}31G(2}df,p\mathrm{)|6\text{-}31G(}d\mathrm{)}) + c_7\Delta E(\mathrm{MP4|MP4SDQ/6\text{-}31G(}d\mathrm{)}) + c_8\Delta E(\mathrm{QCISD(T)|MP4/6\text{-}31G(}d\mathrm{)}) + E_{\mathrm{SO}} + E_{\mathrm{CC}} \tag{6}$$

$$E(\mathrm{MC\text{-}QCISD}) = c_1E(\mathrm{HF/6\text{-}31G(}d\mathrm{)}) + c_2\Delta E(\mathrm{MP2|HF/6\text{-}31G(}d\mathrm{)}) + c_3\Delta E(\mathrm{MP2/MG3|6\text{-}31G(}d\mathrm{)}) + c_4\Delta E(\mathrm{QCISD|MP2/6\text{-}31G(}d\mathrm{)}) \tag{7}$$

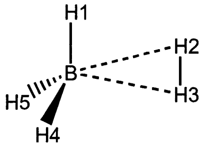
The MG3 (modified G3) basis set denotes the G3large basis set without the core polarization functions.[31] Each of these methods assigns coefficients to each energy difference involved in the linear combination; the coefficients have been optimized to fit the atomization energies of 82 molecules containing first-and-second-row elements.[22] In the MCCM-UT, MC-QCISD, and MCG3 methods, the basis set deficiency has been corrected by the linear combination of the energy difference with optimized coefficients.

The multilevel structure, energy, and Hessian are calculated by using the multilevel 2.1.1 program.[32] This program uses the *Gaussian 98*[30] package to obtain the energy, gradient, and Hessian components and then combines the components to calculate the multilevel energy, gradient, and Hessian. Frequencies were calculated from the Hessian. Single-level Hessians were used with the Newton−Raphson step. In most cases, an HF/6-31G(d,p) Hessian was recalculated every three steps, and this matrix was used in the determination of every Newton−Raphson step for all multilevel optimizations.

3. Results and Discussion

The optimized structures of BH_5 at the QCISD and CCD levels have C_s symmetry. The MCCM level of theory also predicts the C_s structure and the geometrical parameters are listed in Table 1 along with the previous high-level ab initio results.[29] The bond lengths for B−H2 and B−H3 at the QCISD and CCD levels are longer than the corresponding values from the ab initio study, whereas those from the MCCMs are slightly

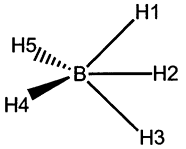
TABLE 1: Geometrical Parameters of BH_5 Optimized at the MCCM Levels along with the High Level ab Initio Results[a]



parameters	QCISD/ TZ2P	CCD/ TZ2P	MC-QCISD	MCCM- UT-CCSD	MCCM- UT-MP4SDQ	MCG3	CCSD(T)/ TZ(3d1f,2p1d)[b]
r(B−H1)	1.198	1.198	1.203	1.196	1.195	1.204	1.202
r(B−H2)	1.472	1.478	1.401	1.401	1.397	1.411	1.422
r(B−H3)	1.484	1.490	1.415	1.416	1.411	1.425	1.436
r(B−H4)	1.191	1.191	1.194	1.187	1.186	1.195	1.194
r(H2−H3)	0.786	0.785	0.808	0.796	0.796	0.805	0.799
θ(H1−B−H2)	80.2	80.3	79.2	79.5	79.5	79.4	79.6
θ(H2−B−H3)	30.8	30.7	33.4	32.8	32.9	33.0	32.5
θ(H4−B−H5)	119.9	119.9	120.1	120.0	120.1	120.1	120.1

[a] The BH_5 structure has C_s symmetry. Lengths are in angstroms, and angles are in degree. [b] Reference 29.

TABLE 2: Geometrical Parameters for the Transition State of Hydrogen Scrambling in BH_5 Optimized at the MCCM Levels along with the High Level ab Initio Results[a]



parameters	QCISD/ TZ2P	CCD/ TZ2P	MC- QCISD	MCCM- UT-CCSD	MCCM- UT-MP4SDQ	MCG3	CCSD(T)/ TZ(3d1f,2p1d)[b]
r(B−H1)	1.268	1.267	1.268	1.260	1.258	1.271	1.270
r(B−H2)	1.250	1.240	1.250	1.242	1.240	1.253	1.251
r(B−H4)	1.180	1.180	1.187	1.181	1.178	1.187	1.187
r(H1−H2)	1.080	1.070	1.089	1.081	1.080	1.088	
θ(H1−B−H2)	50.8	50.6	51.2	51.2	51.2	51.0	
θ(H4−B−H5)	128.1	128.1	128.1	128.1	128.1	128.0	128.1

[a] The TS structure has C_{2v} symmetry. Lengths are in angstroms, and angles are in degree. [b] Reference 29.

TABLE 3: Dissociation Energies of BH_5 and Barrier Height for Hydrogen Scrambling Calculated at Various Levels of Theory[a]

level	D_e	D_o	D_e(fitting)	$V^\ddagger$
QCISD/TZ2P	2.14	−2.69		7.52
CCD/TZ2P	1.89	−2.90		7.57
MC-QCISD	6.15	0.83	6.12	5.44
MCCM-UT-CCSD	5.76	0.37	5.76	5.71
MCCM-UT-MP4SDQ	6.11	0.73	6.09	5.59
MCG3	5.95	0.65	5.92	5.83
G3//QCISD/TZ2P	4.95		5.13	6.10
CCSD(T)/cc-pVQZ//QCISD/TZ2P	5.58		5.74	5.96
CCSD+T(CCSD)/[5s4p3d1f/4s2p1d]//MP2/[3s2p1d/2s1p][b]	5.4	0.9		7.2
CCSD(T)/TZ2P[c]	3.32	0.72		6.79
CCSD(T)/DZP[c]	0.89	0.19		6.38
CCSD(T)/TZ(3d1f,2p1d)[c]	5.26	0.36		6.11
CCSD(T)/TZ(3d1f1g,2p1d)//CCSD(T)/TZ(3d1f,2p1d)[c]	5.82	0.92		5.65

[a] Energies are in kcal/mol. D_e and D_o are dissociation energies from the equilibrium structure and from the zero-point energy level, respectively. $V^\ddagger$ is the barrier height for the hydrogen scrambling of BH_5. [b] Reference 33. [c] Reference 29. Zero-point energies are scaled by 0.95.

shorter. The geometrical parameters from the MCCMs show good agreement with those from the CCSD(T)/TZ(3d1f,2p1d) level. In particular, the structure from the MCG3 method agrees very well. Table 2 lists the geometrical parameters for the transition state (TS) of hydrogen scrambling. Both QCISD and CCD levels predict the TS structure with C_{2v} symmetry, which is consistent with the CCSD(T)/TZ(3d1f,2p1d) level. All MCCMs used in this study give the same symmetry for the TS too. The TS structures from the MCG3 and MC-QCISD methods agree almost perfectly with that from CCSD(T)/TZ(3d1f,2p1d) level.

Table 3 lists the dissociation energies of BH_5 and barrier heights of hydrogen scrambling calculated at various levels of theory. The D_e values from the QCISD and CCD levels are 2.14 and 1.89 kcal/mol, respectively, which are too small, and the $V^\ddagger$ values are 7.52 and 7.57 kcal/mol, respectively. These levels predict too weak binding with long distance between BH_3 and H_2 moieties. Schreiner et al.[29] have performed various levels of ab initio calculations for the BH_5 systems. They found that geometry and energy of BH_5 depend very much on the level of theory and the size of basis sets. The D_e values at the CCSD(T) level with TZ2P and DZP basis sets were 3.32 and 0.82 kcal/mol, respectively. They have reported 5.82 and 5.65 kcal/mol for the D_e and $V^\ddagger$ values, respectively, at the CCSD(T)/TZ(3d1f1g,2p1d)//CCSD(T)/TZ(3d1f,2p1d) level, which is the highest level of theory used so far. They

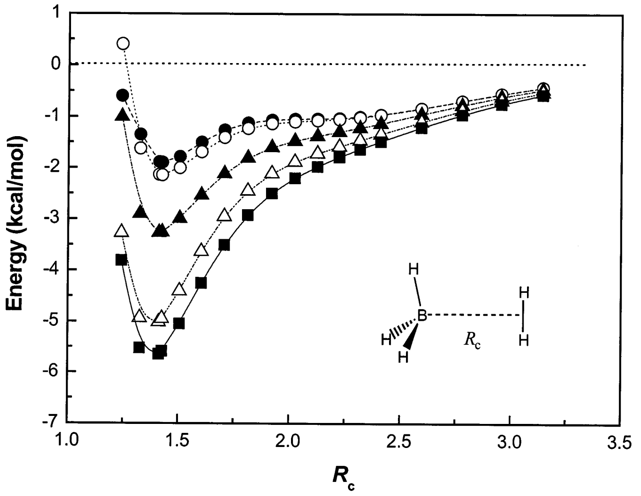


Figure 1. Potential energy curves along the dissociation coordinate of BH_5. The partially optimized structures at the QCISD/TZ2P level were used. The closed circles, open circles, closed triangles, open triangles, and closed squares are obtained at the CCD/TZ2P, QCISD/TZ2P, QCISD(T)//QCISD/TZ2P, G3//QCISD/TZ2P, and CCSD(T)/cc-pVQZ//QCISD/TZ2P levels, respectively.

estimated about 0.14 kcal/mol for the BSSE in the dissociation energy, which is quite small. The D_e and $V^{\ddagger}$ values at the CCSD(T)/TZ(3d1f,2p1d) level were 5.26 and 6.11 kcal/mol, respectively. Adding one set of boron g-type function increases the dissociation energy and decreases the barrier height. Considering higher electron correlation and using larger basis sets seem to increase the dissociation energy and decrease the barrier height.

All D_e and $V^{\ddagger}$ values from the MCCM agree very well with those from the CCSD(T)/TZ(3d1f1g,2p1d) level. In particular, the MCCM-UT-CCSD values agree almost perfectly. The G3//QCISD/TZ2P level underestimates the dissociation energy and slightly overestimates the barrier height. The D_o value at the CCSD(T)/TZ(3d1f1g,2p1d) level is 0.92 kcal/mol, which is larger than all of the MCCM values. Schreiner et al.[29] have obtained zero-point energies from frequencies calculated at the CCST(T)/TZ2P level and scaled by 0.95. The MCCM frequencies are not scaled. If we scaled these frequencies by 0.95, the D_o values would be increased by about 0.27 kcal/mol, and then our MCCM values agree quite well with the results by Schreiner et al.

The potential energy curve along the dissociation coordinate calculated at the QCISD/TZ2P, CCD/TZ2P, QCISD(T)//QCISD/TZ2P, CCSD(T)/cc-pVQZ//QCISD/TZ2P, and G3//QCISD/TZ2P levels are shown in Figure 1. We have plotted the potential energy with respect to the distance between B atom and the center of H_2 unit, R_c, as the dissociation coordinate. The QCISD and CCD levels show an unusually flat region on the potential energy curve where R_c is between 1.6 and 2.4 Å. Using a higher level of electron correlation increases the well depth and improves the shape of the curve, as shown in the curve at the QCISD(T)//QCISD/TZ2P level, but this curve is still far from the standard Morse type potential curve. We have performed the CCSD(T)/cc-pVQZ//QCISD/TZ2P calculations, and the potential curve is very smooth without the flat region. Not only high correlation level but also larger basis sets seem mandatory for the high quality potential energy surface. The potential energy curves plotted at the MCCM levels are shown in Figure 2. These potential curves are quite consistent with each other, and the flat region is disappeared. However, these curves cannot be fitted into a single Morse type function either. It is not surprising because the reaction coordinate parameter, R_c, is not defined as a single bond distance. So we made an equation with two range parameters for the Morse type function to fit the potential curves, as shown in eq 8:

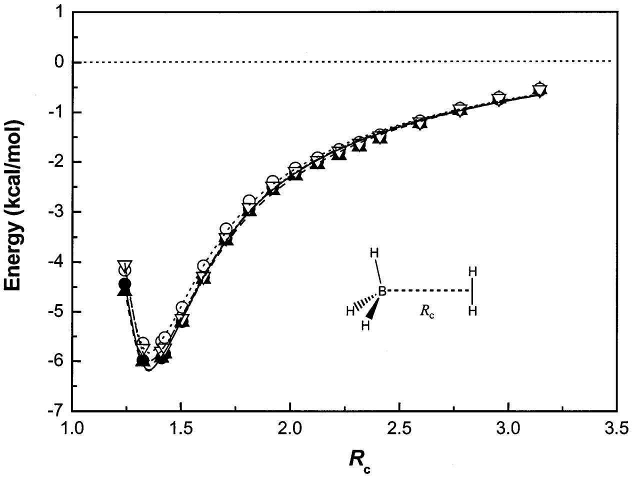


Figure 2. Potential energy curves along the dissociation coordinate of BH_5. Potential energies were calculated by using the partially optimized structure at the QCISD/TZ2P level. Lines passed through the points are fitted to eq 2. The closed circles, open circles, closed triangles, and open inverted triangles are from the MC-QCISD, MCCM-UT-CCSD, MCCM-UT-MP4SDQ, and MCG3 methods, respectively. The lines passing through the point are from the best fit of eq 8.

$$V = D_e[[1 - a\exp\{-\alpha_1(R_c - R_e)\} - (1 - a)\exp\{-\alpha_2(R_c - R_e)\}]^2 - 1] \quad (8)$$

In this equation, α_1 and α_2 are range parameters, R_e is the minimum of the potential energy curve, and a and $(1 - a)$ control the relative importance of two terms with range parameters. The estimated D_e values from eq 8 are listed in Table 3, and these values at the MCCM levels are almost identical to the optimized D_e values. The R_e values are 1.351, 1.351, 1.348, and 1.360 Å at the MC-QCISD, MCCM-UT-CCSD, MCCM-UT-MP4SDQ, and MCG3 levels, respectively.

Although the G3 method cannot be used to calculate the potential energy curve for the dissociation of a molecule to atomic species because of the HLC term, it is okay for BH_5 dissociation because it dissociates into two molecular species, BH_3 and H_2. The potential curve from the G3//QCISD/TZ2P method is shown in Figure 1. This curve is better in shape than those at the QCISD or QCISD(T) levels. We have fitted the G3 potential curve to eq 8 and obtained 5.13 kcal/mol and 1.360 Å for the D_e and R_e values, respectively. The R_e value is the same as that from the MCG3 method; however, the D_e value is smaller than the MCCM and the CCSD(T)/TZ(3d1f1g,2p1d) values. The potential curve at the CCSD(T)/cc-pVQZ//QCISD/TZ2P level was also fitted to eq 8. This curve is lower in energy than the G3 curve. The well depth from the curve fitting is increased to about 5.74 kcal/mol, and the R_e value is 1.366 Å. This well depth is almost identical to the D_e value at the CCSD(T)/TZ(3d1f1g,2p1d) level. These results suggest that at least the CCSD(T)/cc-pVQZ level of theory is required to generate a reasonably accurate potential energy surface of the BH_5 dissociation. The single-point energy calculation at the MCG3 level, which is the highest level among the MCCMs used in this study, takes about 43 s of the CPU time on the Compaq GS320 computer, whereas the same calculation at the CCSD(T)/cc-pVQZ level takes about 12400 s. The MCG3 calculation is about 280 times faster than the CCSD(T)/cc-pVQZ calculation. The MCCM-UT-MP4SDQ and MCCM-UT-CCSD are even faster than the MCG3, and the relative computing times among MCCMs have been reported previously.[20]

Figures 1 and 2 show quite clearly that the MCCMs can correct the incompleteness of QCISD and CCD level with TZ2P basis sets for the potential energy surface of BH_5 dissociation. This method is even superior to the QCISD(T)/TZ2P and G3 methods. It is interesting to note that only experimental atomization energies are used to adjust the coefficients of the MCCM. No experimental data for weak chemical interactions are used. The MCCMs have been tested successfully to reproduce the structures and energies of hydrogen-bonded dimers[24] and hydrated proton clusters[25] and proton affinities of molecules.[23] This study and previous results suggest that the MCCM could be applied to reproduce many other chemical properties than the atomization energy. Another important observation is that the most accurate method among the MCCMs for the atomization energy is not necessarily the case for other chemical properties.[24] In this study, all four MCCMs give almost the same results in the dissociation energy and barrier height. The Maximum deviation within these four methods is only 0.4 kcal/mol for both dissociation energy and barrier height. The MCCM-UT-CCSD agrees the best with the CCSD(T)/TZ(3d1f1g,2p1d) level, and all MCCMs take much less computing time.

4. Conclusions

We have calculated structures and energies of BH_5 and the TS for the hydrogen scrambling using recently developed multicoefficient correlated quantum mechanical methods. Our results agree very well with those from the CCSD(T)/TZ(3d1f1g,2p1d) level. We have also calculated the potential energy curves for the dissociation of BH_5 into BH_3 and H_2. The QCISD and CCD levels with TZ2P basis sets produce a flat region on the potential curves, where the reaction coordinate parameter, R_c, is around 1.6 and 2.4 Å. It would be necessary to use the CCSD(T)/TZ(3d1f1g,2p1d) level of theory to generate the reasonable potential energy curve for the BH_5 dissociation. The lower levels of theory were unable to give correct potential curves, whereas the MCCM generates very good potential energy curves and requires much less computing resources than the CCSD(T)/TZ(3d1f1g,2p1d) and CCSD(T)/cc-pVQZ levels.

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