

Breaking Bonds of Open-Shell Species with the Restricted Open-Shell Size Extensive Left Eigenstate Completely Renormalized Coupled-Cluster Method

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Received: July 8, 2008; Revised Manuscript Received: August 25, 2008

The recently developed restricted open-shell, size extensive, left eigenstate, completely renormalized (CR), coupled-cluster (CC) singles (S), doubles (D), and noniterative triples (T) approach, termed CR-CC(2,3) and abbreviated in this paper as ROCCL, is compared with the unrestricted CCSD(T) [UCCSD(T)] and multireference second-order perturbation theory (MRMP2) methods to assess the accuracy of the calculated potential energy surfaces (PESs) of eight single bond-breaking reactions of open-shell species that consist of C, H, Si, and Cl; these types of reactions are interesting because they account for part of the gas-phase chemistry in the silicon carbide chemical vapor deposition. The full configuration interaction (FCI) and multireference configuration interaction with Davidson quadruples correction [MRCI(Q)] methods are used as benchmark methods to evaluate the accuracy of the ROCCL, UCCSD(T), and MRMP2 PESs. The ROCCL PESs are found to be in reasonable agreement with the corresponding FCI or MRCI(Q) PESs in the entire region $R = 1 - 3R_e$ for all of the studied bond-breaking reactions. The ROCCL PESs have smaller nonparallelity error (NPE) than the UCCSD(T) ones and are comparable to those obtained with MRMP2. Both the ROCCL and UCCSD(T) PESs have significantly smaller reaction energy errors (REE) than the MRMP2 ones. Finally, an efficient strategy is proposed to estimate the ROCCL/cc-pVTZ PESs using an additivity approximation for basis set effects and correlation corrections.

I. Introduction

Accurate potential energy surfaces (PESs) are critical for the understanding of the mechanisms of chemical vapor deposition (CVD) processes. CVD often takes place at such a high temperature that bond-breaking reactions of open-shell species cannot be simply omitted without being carefully studied. For example, in the silicon carbide CVD in which CH_3SiCl_3 is used as a precursor, $\text{SiCl}_3 \rightarrow \text{SiCl}_2 + \text{Cl}$ may be of importance because a significant amount of SiCl_3 is produced through the predominant decomposition pathway $\text{CH}_3\text{SiCl}_3 \rightarrow \text{CH}_3 + \text{SiCl}_3$ and because the $\text{SiCl}_3 \rightarrow \text{SiCl}_2 + \text{Cl}$ reaction is favored by entropy at high CVD temperatures.^{1,2} Multireference methods such as the complete active space self-consistent field (CASSCF), multireference configuration interaction (MRCI),^{3,4} and multireference second-order perturbation theory (MRMP2)^{5,6} methods have often been used to study the bond-breaking reactions of open-shell species. However, the multireference methods have their limitations. The CASSCF method does not recover the dynamic correlation energy and it is computationally difficult for an active space that has more than 16 active

electrons and 16 active orbitals. Multireference configuration interaction (MRCI) calculations that are based on single and double excitations from the CASSCF determinants are computationally challenging for all but small systems. Multireference second-order perturbation theory (MRMP2) recovers dynamic correlation energy in a perturbative way; it is less computationally demanding than MRCI at the cost of accuracy. Neither MRCI nor MRMP2 is rigorously size extensive;⁷ this is a concern for the prediction of bond-breaking reaction energies and for examining larger systems in general, where the lack of extensivity leads to loss of accuracy as the system size increases. Although one can formulate size extensive multireference many-body perturbation theory methods⁸ and although there are ways to approximately correct MRCI for the lack of size extensivity, either through multireference extensions^{9,10} of the well-known Davidson corrections^{11,12} or through the more intrinsic modifications of the CI Hamiltonian matrices,¹³ no multireference approach currently matches the ease of use of a single-reference calculation. Rigorously size extensive multireference coupled-cluster (MRCC) methods that are suitable for bond breaking exist,^{14–16} and recent years have witnessed renewed interest in the development and implementation of computationally tractable MRCC schemes that maintain size extensivity.^{17–27} However, in addition to the practical and formal challenges of the existing MRCC schemes and their relatively large computer costs (similar to the costs of the equivalent MRCI calculations),

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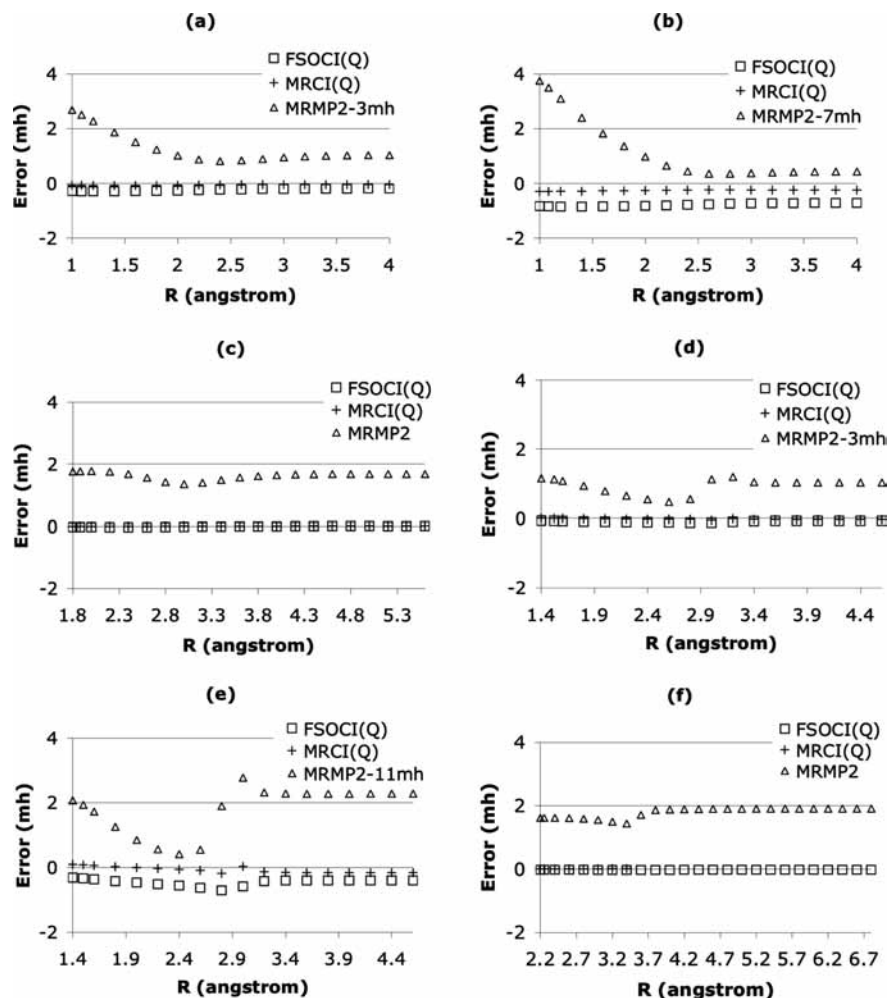


Figure 1. FSOCI(Q), MRCI(Q), and MRMP2 errors relative to the FCI PES. Open shell species [basis set]: (a) $\text{H}_2\text{C}-\text{H}$ [6-31G]; (b) $\text{H}_2\text{C}-\text{H}$ [6-31G(d)]; (c) $\text{H}_2\text{C}-\text{Cl}$ (MIX); (d) $\text{H}_2\text{Si}-\text{H}$ [6-31G]; (e) $\text{H}_2\text{Si}-\text{H}$ [6-31G(d)]; (f) $\text{H}_2\text{Si}-\text{Cl}$ (MIX).

TABLE 1: FSOCI(Q) and MRCI(Q) Nonparallelity Errors (NPE), Standard Deviation Errors (STD), and Reaction Energy Errors (REE) Relative to the FCI PES (mhartree Units)^a

species	basis	NPE		STD		REE	
		FSOCI (Q)	MRCI (Q)	FSOCI (Q)	MRCI (Q)	FSOCI (Q)	MRCI (Q)
$\text{H}_2\text{C}-\text{H}$	6-31G	0.101	0.040	0.041	0.016	0.097	0.032
	6-31G(d)	0.137	0.051	0.055	0.020	0.125	0.048
$\text{H}_2\text{C}-\text{Cl}$	MIX	0.041	0.023	0.016	0.009	0.036	0.022
$\text{H}_2\text{Si}-\text{H}$	6-31G	0.061	0.056	0.020	0.015	0.001	-0.033
	6-31G(d)	0.398	0.282	0.106	0.099	-0.062	-0.242
$\text{H}_2\text{Si}-\text{Cl}$	MIX	0.008	N.A.	0.002	N.A.	-0.004	N.A.

^a The MRCI(Q) numbers are not available for $\text{H}_2\text{Si}-\text{Cl}$ due to CASSCF convergence problems in the $R(\text{Si}-\text{Cl}) = 3.4-6.8$ Å region.

it is not always straightforward to determine a tractable reference space for MRCC and active-space CC calculations. In general, the selection of the active space for multireference calculations must be done with great care to obtain consistent reaction energies. Therefore, it is desirable to apply an accurate, size-extensive, and easy-to-use single-reference method to break the bonds of both closed-shell and open-shell species, when a large number of potential energy surfaces (PESs) of the bond-breaking reactions of open-shell species need to be calculated, especially when a comprehensive understanding of high-temperature chemistry in a CVD process is of interest.

TABLE 2: MRCI(Q) NPE, STD and REE Relative to the FSOCI(Q) PES (mhartree Units)

species	basis	NPE	STD	REE
$\text{H}_2\text{C}-\text{H}$	cc-pVDZ	0.178	0.070	-0.134
	cc-pVTZ	0.348	0.114	0.017
$\text{H}_2\text{C}-\text{Cl}$	6-31G	0.561	0.229	-0.561
	6-31G(d)	1.570	0.544	-1.371
$\text{H}_2\text{Si}-\text{H}$	cc-pVDZ	1.634	0.561	-1.414
	cc-pVTZ	0.411	0.156	-0.255
$\text{H}_2\text{Si}-\text{Cl}$	6-31G	0.756	0.287	-0.406
	6-31G	0.625	0.245	-0.489
	6-31G(d)	1.450	0.588	-1.394
	cc-pVDZ	1.531	0.596	-1.458

Piecuch et al. developed a restricted-Hartree-Fock-based, size extensive, left eigenstate completely renormalized (CR) coupled-cluster (CC) singles (S), doubles (D), and noniterative triples (T) approach, termed CR-CCSD(T)_L or CR-CC(2,3)²⁸⁻³⁰ and abbreviated CCL.³¹ The CCL method belongs to a larger CR-CC(*m*, *n*) family based on the biorthogonal formulation^{29,30} of the method of moments coupled-cluster equations.³²⁻³⁵ CCL has been shown to reproduce full configuration interaction (FCI) PESs with small errors for the single-bond-breaking reactions of nine closed-shell C-H-Si-Cl molecules.²⁹⁻³¹ The restricted open-shell CCL (ROCCL) method has been shown to properly break the OH and F_2^+ bonds within reasonable accuracy.²⁸ The nonparallelity errors (NPE, defined²⁸ as the difference between the most positive and most negative signed errors along a given

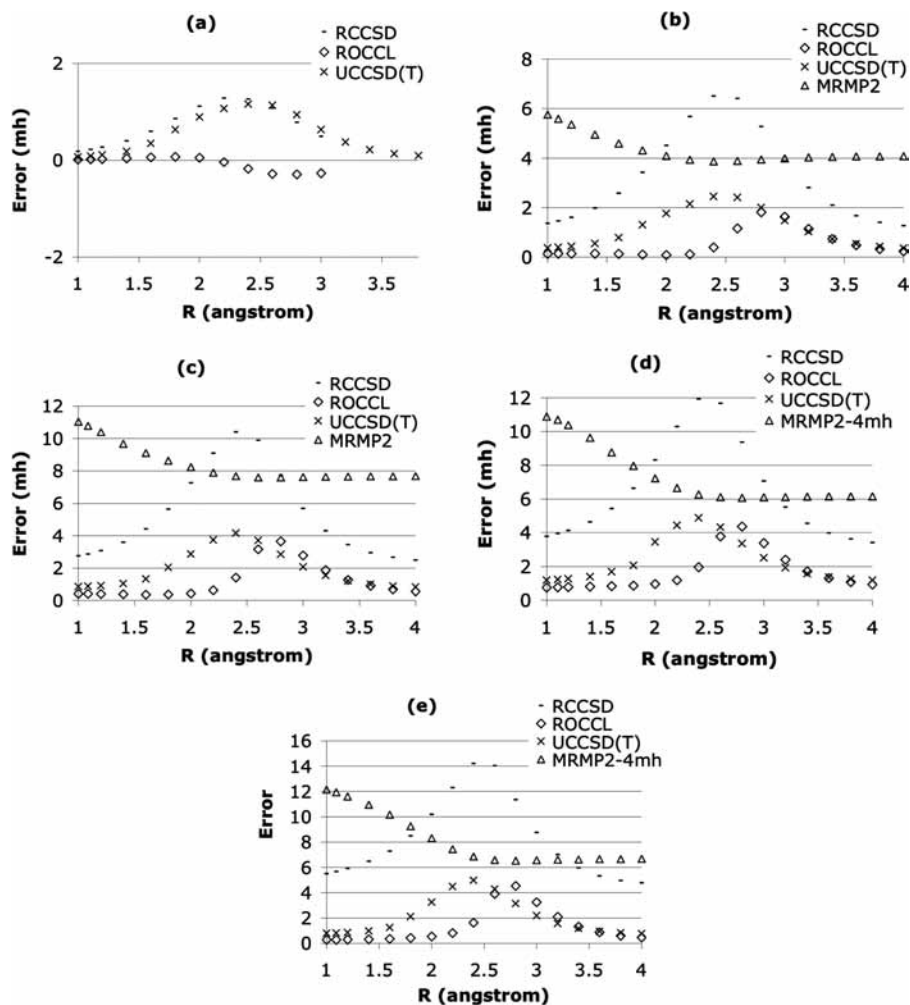


Figure 2. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{C}-\text{H} \rightarrow {}^3\text{CH}_2 + \text{H}$. Basis sets: (a) MINI; (b) 6-31G; (c) 6-31G(d); (d) cc-pVDZ; (e) cc-pVTZ.

potential energy curve) of the OH (F_2^+) bond-breaking reactions are 2.8 (8.4) mhartree relative to FCI. Włoch et al.²⁸ have also demonstrated the negligible dependence of the ROCCL energy on the canonicalization method of the ROHF orbitals, on the order of 10^{-5} hartree, and the potential usefulness of the ROCCL approach in studies of singlet–triplet gaps in magnetic/biradical systems.

The present paper investigates the accuracy of the ROCCL method for breaking the bonds of open-shell species including $\text{H}_2\text{C}-\text{H}$, $\text{H}_2\text{C}-\text{Cl}$, $\text{H}_2\text{C}-\text{CH}_3$, $\text{H}_2\text{C}-\text{SiH}_3$, $\text{H}_2\text{Si}-\text{H}$, $\text{H}_2\text{Si}-\text{Cl}$, $\text{H}_2\text{Si}-\text{CH}_3$, and $\text{H}_2\text{Si}-\text{SiH}_3$, each of which has one less H atom than the closed shell molecules studied previously.³¹ The accuracy of the ROCCL PESs is compared with that of the conventional UCCSD(T)³⁶ method. The ROCCL potential energy error curves are also compared with the MRMP2 ones. This work also demonstrates that the approximation of the additivity of basis set effects and correlation corrections can be used to estimate the ROCCL/cc-pVTZ PESs for the bond-breaking reactions of various C–H–Si–Cl systems with the computational cost of ROCCL/cc-pVDZ and MP2/cc-pVTZ calculations.

There have been several benchmark studies illustrating the ability of the CR-CC(2,3) or CCL method to describe single bond breaking on singlet PESs and biradicals,^{29–31,37–41} but little is known about the performance of the CCL approach in calculations of bond breaking in radical species, particularly for the large class of systems examined in this work. In particular,

nothing is known about the performance of the ROCCL method²⁸ when compared to the conventional UCCSD(T) approach, which is usually the method of choice in high-accuracy studies of radical species. One of the main issues of this work is to determine if ROCCL can improve the overall shape of the PESs of radical species along bond breaking coordinates produced by UCCSD(T), particularly in the region of intermediate internuclear separations, and the resulting dissociation energies, where UCCSD(T) is widely recognized as a “gold standard.”

The paper is organized as follows. The Computational Details section covers the construction of the ROCCL, UCCSD(T), and MRMP2 PESs, the benchmark methods, and the PES error indicators. The Results and Discussion section considers the evaluation of the accuracy of the benchmark methods and the ROCCL, UCCSD(T), and MRMP2 energy errors. Conclusions are drawn in the last section.

II. Computational Details

A. PES Calculations. The ROCCL, UCCSD(T), and MRMP2 PESs are calculated with five different basis sets, MINI,⁴² 6-31G,^{43–45} 6-31G(d),^{43–45} cc-pVDZ,^{46,47} and cc-pVTZ,^{46,47} for the bond-breaking reactions of the eight open-shell species noted above. The exceptions are for the CH_2-Cl and SiH_2-Cl PESs, for which the MINI basis set is replaced with a mixed basis set (MIX) that uses the MINI basis for C, Si, Cl and 6-311G for the H atoms. The ROCCL, UCCSD(T), and MRMP2 methods

TABLE 3: ROCCL, UCCSD(T), and MRMP2 NPE, STD and REE Relative to the MRCI(Q) PES (mhartree Units)^{a,b}

species	basis	NPE			STD			REE		
		ROCCL	UCCSD(T)	MRMP2	ROCCL	UCCSD(T)	MRMP2	ROCCL	UCCSD(T)	MRMP2
H ₂ C–H	MINI	0.366	1.093	N.A.	0.146	0.431	N.A.	-0.313	0.851	N.A.
	6-31G	1.725	2.081	1.883	0.565	0.766	0.627	0.104	-0.035	-1.507
	6-31G(d)	3.279	3.339	3.447	1.072	1.160	1.226	0.152	-0.052	-3.114
	cc-pVDZ	3.621	3.699	4.807	1.162	1.286	1.832	0.170	-0.040	-4.529
	cc-pVTZ	4.256	4.223	5.613	1.365	1.455	2.181	0.181	-0.062	-5.276
H ₂ C–Cl	MIX	2.022	1.965	0.436	0.624	0.754	0.125	-0.840	-1.118	-0.114
	6-31G	3.772	2.674	0.832	1.175	0.957	0.293	0.111	-0.421	0.123
	6-31G(d)	6.787	6.146	2.694	1.919	1.956	0.777	0.583	0.248	-1.519
	cc-pVDZ	7.112	6.705	2.875	2.029	2.072	0.855	0.643	0.423	-1.653
	cc-pVTZ	8.367	7.794	4.646	2.398	2.327	1.410	0.582	1.165	-2.879
H ₂ C–CH ₃	MINI	0.301	2.543	N.A.	0.197	0.849	N.A.	-0.326	0.300	N.A.
	6-31G	3.126	4.023	1.176	0.981	1.401	0.401	0.160	-0.039	-0.753
H ₂ C–SiH ₃	MINI	0.412	1.814	N.A.	0.127	0.666	N.A.	0.064	0.017	N.A.
	6-31G	2.681	3.142	1.553	0.821	1.069	0.539	-0.136	-0.236	-1.272
H ₂ Si–H	MINI	0.237	0.443	N.A.	0.063	0.142	N.A.	0.049	0.063	N.A.
	6-31G	0.526	0.801	0.697	0.151	0.277	0.228	0.041	0.035	-0.059
	6-31G(d)	1.061	1.450	2.271	0.239	0.366	0.767	0.300	0.509	0.585
	cc-pVDZ	0.923	1.100	3.128	0.212	0.315	0.847	0.245	0.236	-0.822
	cc-pVTZ	1.132	2.092	3.310	0.295	0.547	0.873	0.584	0.577	-0.842
H ₂ Si–Cl	MIX	0.744	1.377	0.478	0.225	0.406	0.163	-0.114	-0.342	0.294
	6-31G	0.682	2.094	1.917	0.175	0.592	0.565	0.463	0.346	-1.870
	6-31G(d)	1.917	3.616	3.302	0.583	0.842	1.308	0.054	0.474	2.034
	cc-pVDZ	1.833	3.661	4.170	0.543	0.814	1.688	0.068	0.499	2.823
	cc-pVTZ	2.705	3.600	4.472	0.801	0.764	1.604	-1.013	0.221	2.006
H ₂ Si–CH ₃	MINI	0.392	0.696	N.A.	0.127	0.235	N.A.	-0.040	-0.110	N.A.
	6-31G	0.434	0.765	1.288	0.114	0.226	0.321	-0.054	-0.031	-0.740
H ₂ Si–SiH ₃	MINI	0.485	1.991	N.A.	0.158	0.571	N.A.	-0.046	0.000	N.A.
	6-31G	1.510	2.048	0.797	0.357	0.545	0.184	-0.077	-0.115	0.103
6-31G unsigned average		1.807	2.204	1.268	0.542	0.729	0.395	0.143	0.157	0.803
cc-pVTZ unsigned average		4.115	4.427	4.510	1.215	1.273	1.517	0.590	0.506	2.751

^a FCI is the benchmark method with the MINI basis set. ^b Due to ROHF convergence problems, ROCCL/MINI numbers are not available in the regions of $R(\text{H}_2\text{C}-\text{H}) > 3.0 \text{ \AA}$, $R(\text{H}_2\text{C}-\text{CH}_3) > 3.6 \text{ \AA}$, $R(\text{H}_2\text{C}-\text{SiH}_3) > 4.6 \text{ \AA}$, $R(\text{H}_2\text{Si}-\text{H}) = 3.0-3.2 \text{ \AA}$, $R(\text{H}_2\text{Si}-\text{CH}_3) = 3.4 \text{ \AA}$, or $R(\text{H}_2\text{Si}-\text{SiH}_3) = 4.0-4.2 \text{ \AA}$.

are not evaluated with the 6-31G(d), cc-pVDZ, or cc-pVTZ basis set for the H₂C(Si)-C(Si)H₃ bond-breaking reactions due to the excessive computational cost of the benchmark MRCI(Q) calculations, where “Q” refers to the Davidson correction.^{11,12}

The PESs are constructed by sampling the breaking bond distances at every 0.2 Å from slightly shorter than the equilibrium bond length (R_e) to slightly larger than $3R_e$. If the last two structures at $\sim 3R_e$ have an energy difference larger than 0.16 mhartree (0.1 kcal/mol), a few more structures with longer bond distances are studied until the 0.16 mhartree threshold is passed. This is to ensure that the two fragments on the product side have negligible interaction and the bond can be considered to be broken. FCI is used to optimize the structures on the H₂C(Si)-H bond-breaking reaction PESs with the MINI, 6-31G, and 6-31G(d) basis sets, on the H₂C(Si)-Cl PESs with the MIX basis set, and on the H₂C(Si)-C(Si)H₃ PESs with the MINI basis set. Full-valence CASSCF is used as the optimization method for cases for which the FCI optimization cannot be done.

B. Benchmark Methods. FCI is used as the benchmark when the MINI basis set is used, or when there are no external orbitals for MRCI calculations. Otherwise, internally contracted MRCI(Q)^{3,4} is used as the benchmark method. MRCI(Q) is shown in section III to be capable of reproducing the FCI and FSOCI(Q) results. FSOCI(Q) is the full second-order configuration interaction method with a Davidson quadruples correction; it includes all determinants from single and double excitations out of the CASSCF determinants without internal contraction. All MRCI and MRMP2 calculations are based on full valence CASSCF zeroth-order wave functions.

The frozen core approximation is used in all of the benchmark calculations and also in the ROCCL, UCCSD(T), and MRMP2 calculations.

C. Accuracy Evaluation. The accuracy of the ROCCL, UCCSD(T), and MRMP2 PESs is evaluated using three different indicators: the nonparallelity error (NPE), the standard deviation error (STD), and the reaction energy error (REE).

The nonparallelity error (NPE) is calculated using

$$\text{NPE} = \max[\text{Err}(R_1), \text{Err}(R_2), \dots, \text{Err}(R_N)] - \min[\text{Err}(R_1), \text{Err}(R_2), \dots, \text{Err}(R_N)] \quad (1)$$

where R_i is the set of reaction coordinates of the i th point on the PES, N is the total number of sampled structures along the PES, and $\text{Err}(R_i)$ is the energy of structure R_i calculated by the evaluated method minus the corresponding benchmark energy.

The standard deviation error (STD) is calculated using

$$\text{STD} = \sqrt{\frac{1}{N} \left(\sum_{i=1}^N [\text{Err}(R_i)]^2 - \left\{ \sum_{i=1}^N |\text{Err}(R_i)| \right\}^2 \right)} \quad (2)$$

The reaction energy error (REE) is calculated with

$$\text{REE} = \text{Err}(R_N) - \text{Err}(R_e) \quad (3)$$

where R_N is the structure with the largest bond distance (often $\sim 3R_e$) along the PES of the studied bond-breaking reaction. The REE values can be negative and NPE and STD are always non-negative by their definitions.

In the RCCSD, ROCCL, and UCCSD(T) PESs with the MINI basis set, one to several energies are missing due to HF

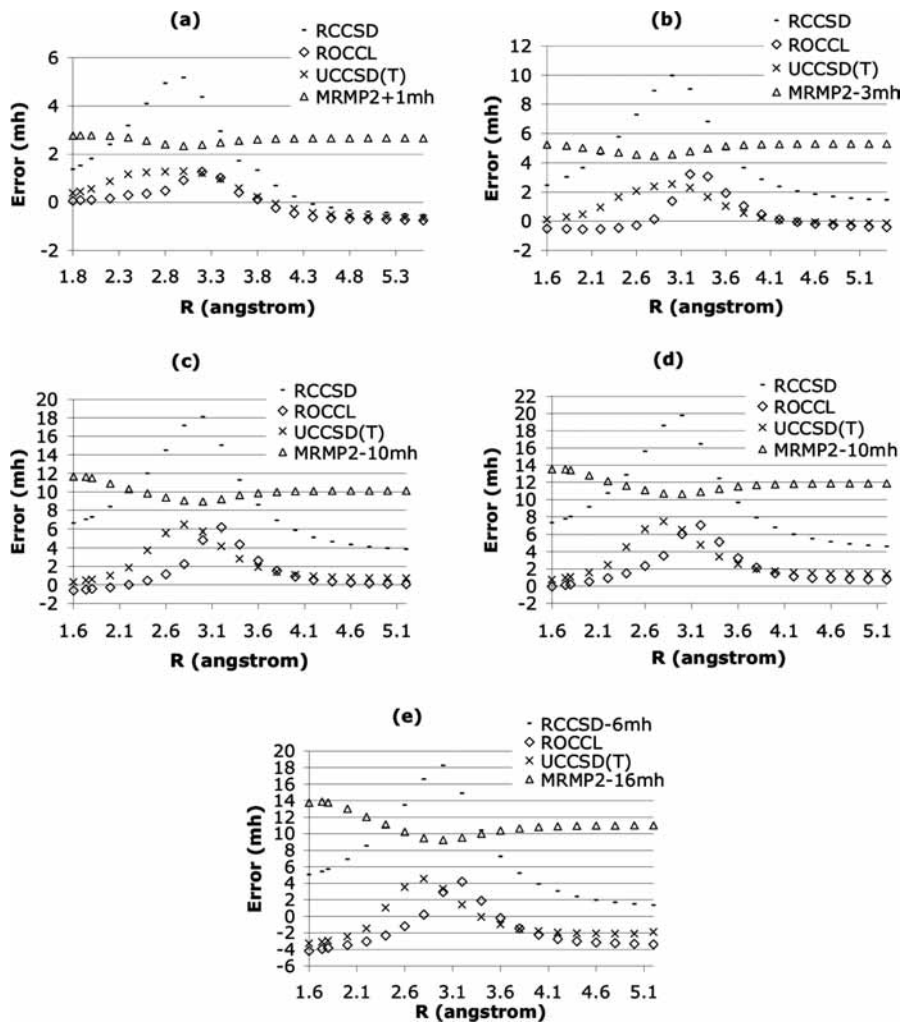


Figure 3. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{C}-\text{Cl} \rightarrow {}^3\text{CH}_2 + \text{Cl}$. Basis sets: (a) MIX; (b) 6-31G; (c) 6-31G(d); (d) cc-pVDZ; (e) cc-pVTZ.

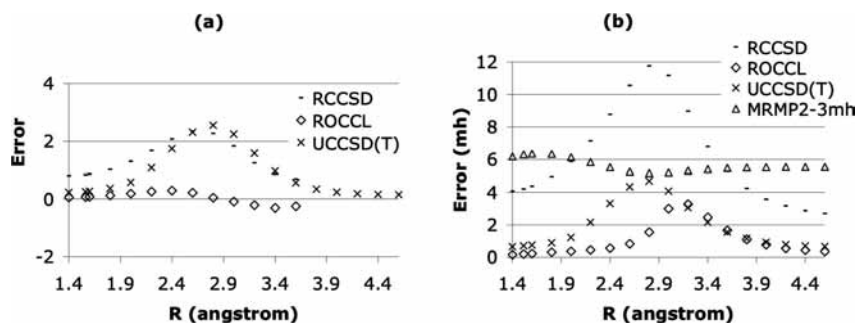


Figure 4. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{C}-\text{CH}_3 \rightarrow {}^3\text{CH}_2 + \text{CH}_3$. Basis sets: (a) MINI; (b) 6-31G.

convergence problems. The NPE, STD, and REE are calculated with only the available data in such cases.

The ROCCL, CASSCF, MRMP2, FSOCI(Q), and FCI calculations were performed using the GAMESS package;^{48,49} the internally contracted MRCI(Q) calculations employed the MOLPRO package;⁵⁰ and the UCCSD(T) calculations used the ACES2⁵¹ and Gaussian 94⁵² packages.

III. Results and Discussion

A. Evaluation of MRCI(Q) for Small Systems. In previous papers,^{28,29,30} MRCI(Q) was used as the benchmark method when FCI calculations could not be performed. The same

strategy is employed here, once MRCI(Q) is calibrated with FCI and FSOCI(Q) for small systems. Figure 1 shows the FSOCI(Q) and MRCI(Q) errors relative to the FCI PES. The MRMP2 error curves are also plotted for comparison. Figures 1a and 1b are the energy error curves for the $\text{H}_2\text{C}-\text{H} \rightarrow {}^3\text{CH}_2 + \text{H}$ reaction with two different basis sets, 6-31G and 6-31G(d). The FSOCI(Q) and MRCI(Q) energy error curves are nearly parallel to the horizontal axis in both Figure 1a,b, whereas the MRMP2 error decreases monotonically by ~ 2 mhartree in the $R \approx 1.0-2.5$ Å region and then levels off at larger distances. The FSOCI(Q) and MRCI(Q) energy error curves can be below the horizontal zero axis because these two methods are not

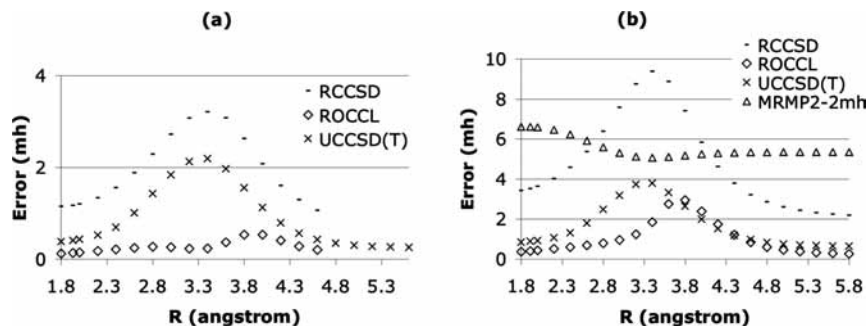


Figure 5. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{C}-\text{SiH}_3 \rightarrow {}^3\text{CH}_2 + \text{SiH}_3$. Basis sets: (a) MINI; (b) 6-31G.

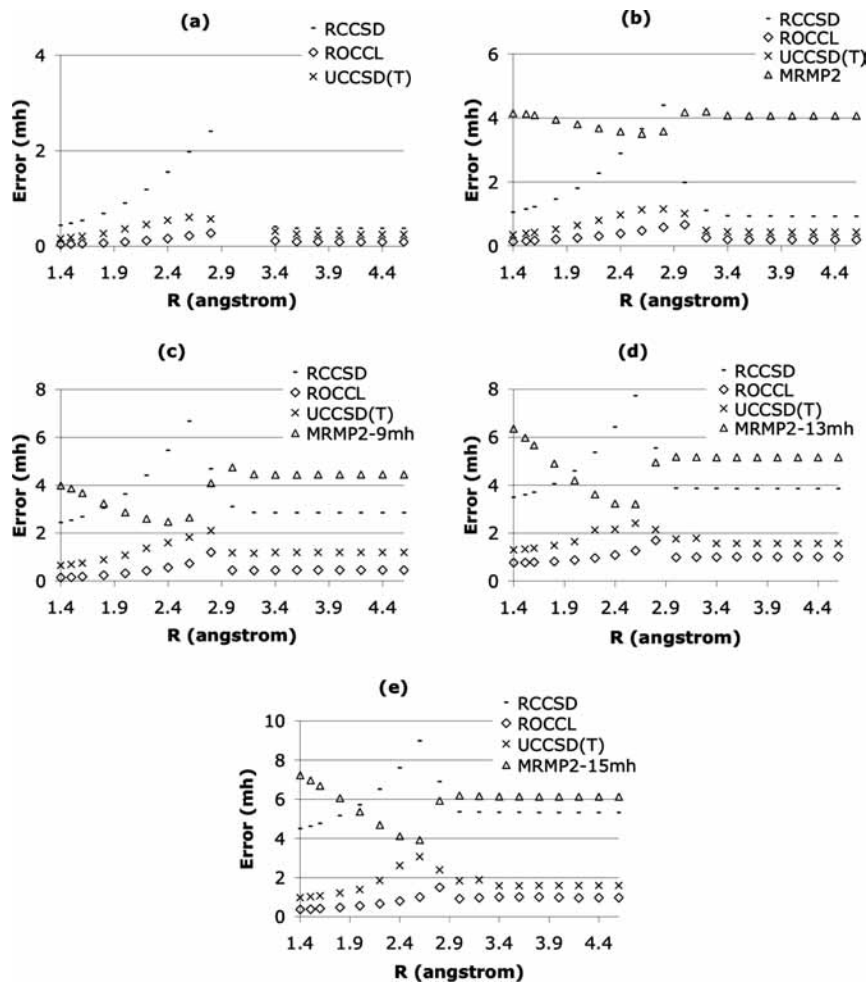


Figure 6. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{Si}-\text{H} \rightarrow {}^1\text{SiH}_2 + \text{H}$. Basis sets: (a) MINI; (b) 6-31G; (c) 6-31G(d); (d) cc-pVDZ; (e) cc-pVTZ.

variational once the (Q) correction is made. Figure 1c shows that the FSOCI(Q) and MRCI(Q) energy error curves are essentially parallel to the horizontal axis for the $\text{H}_2\text{C}-\text{Cl}$ bond-breaking reaction. The MRMP2 error curve is flatter than that for $\text{H}_2\text{C}-\text{H}$. FSOCI(Q) and MRCI(Q) agree well with the FCI PES when the 6-31G basis set is used on the $\text{H}_2\text{Si}-\text{H} \rightarrow {}^1\text{SiH}_2 + \text{H}$ reaction (Figure 1d). The FSOCI(Q) and MRCI(Q) errors are slightly larger when the 6-31G(d) basis set is used for $\text{H}_2\text{Si}-\text{H}$, as shown in Figure 1e. In Figures 1d and 1e the MRMP2 error decreases monotonically in the $R = 1.4-2.4$ Å region but increases in the $R = 2.6-3.0$ Å before leveling off at longer Si-H bond distances; this behavior is due to the transition from the reactant side with a Si-H σ bond and an unpaired electron on Si to the product side with a lone pair on

Si and an unpaired electron on H. FSOCI(Q), MRCI(Q), and MRMP2 are in excellent agreement with FCI for $\text{H}_2\text{Si}-\text{Cl}$ with the MIX basis set (Figure 1f). The MRCI(Q)/MIX energies are not available in the $R = 3.4-6.8$ Å region due to CASSCF convergence problems.

Table 1 lists the NPE, STD, and REE values extracted from the FSOCI(Q) and MRCI(Q) energy error curves in Figures 1a-f. The STD values are within $\sim 30\%$ of the corresponding NPE values with very few exceptions. Therefore, a STD will not be explicitly discussed hereafter unless it deviates significantly from 30% of the corresponding NPE. All of the NPE (REE) values in Table 1 are less than 0.4 (0.3) mhartree. The MRCI(Q) NPE are generally less than the corresponding FSOCI(Q) values. The MRCI(Q) REE amplitudes are smaller

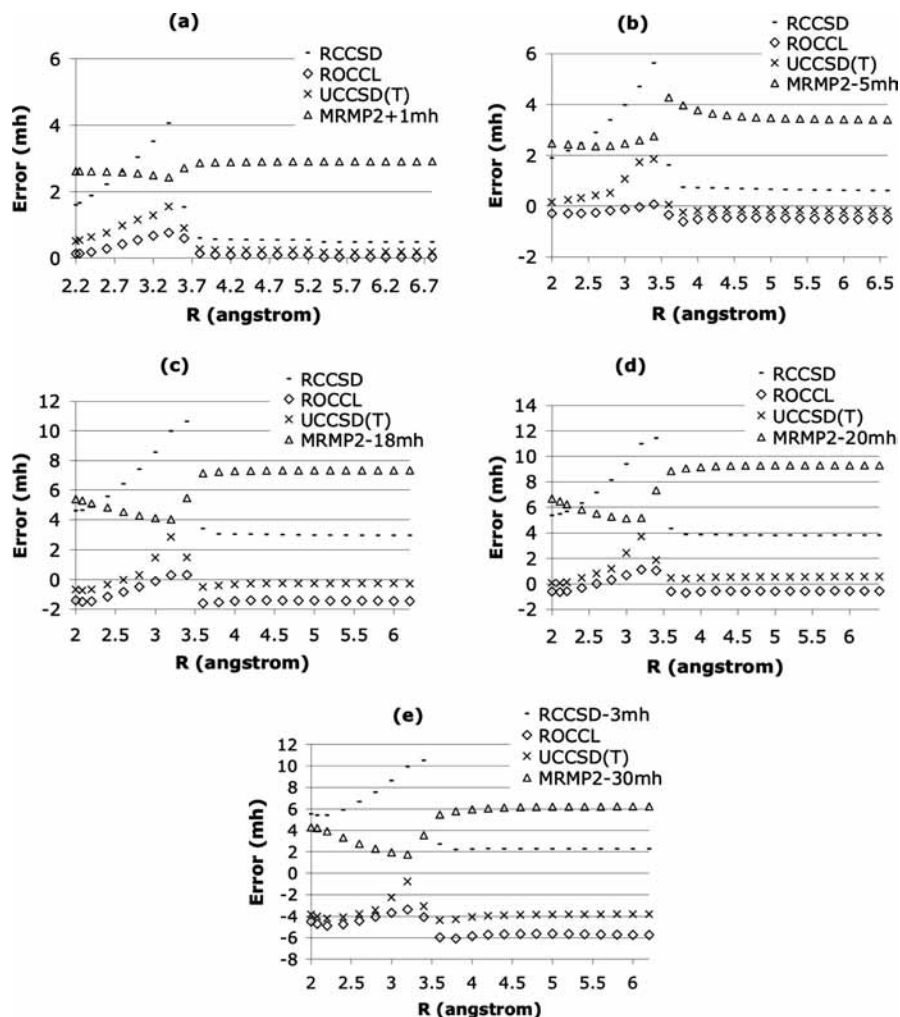


Figure 7. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{Si}-\text{Cl} \rightarrow {}^1\text{SiH}_2 + \text{Cl}$. Basis sets: (a) MIX; (b) 6-31G; (c) 6-31G(d); (d) cc-pVDZ; (e) cc-pVTZ.

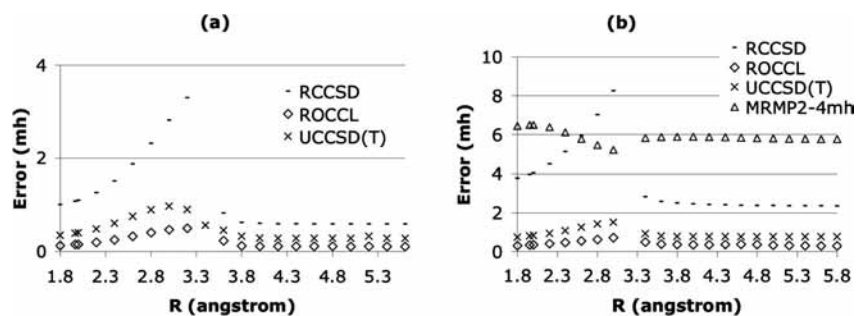


Figure 8. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{Si}-\text{CH}_3 \rightarrow {}^1\text{SiH}_2 + \text{CH}_3$. Basis sets: (a) MINI; (b) 6-31G.

than the corresponding FSOCI(Q) amplitudes for $\text{H}_2\text{C}-\text{H}(\text{Cl})$, but larger for $\text{H}_2\text{Si}-\text{H}(\text{Cl})$. MRCI(Q) is overall slightly more accurate than FSOCI(Q). The FSOCI(Q) and MRCI(Q) energy errors increase with the basis set size. The FSOCI(Q) and MRCI(Q) NPE and REE are significantly smaller than the chemical accuracy of 1 kcal/mol.

The FCI calculations become more computationally formidable with larger active spaces than those used in the calculations described in Figure 1. Therefore, the MRCI(Q) PESs are compared directly with FSOCI(Q) as a reference for the larger basis sets listed in Table 2. The MRCI(Q) NPE relative to FSOCI(Q) increase with the basis size; the MRCI(Q) REE typically show the same trend. However, these errors are

generally less than ~ 1.6 mhartree ≈ 1 kcal/mol, so they are rather small.

In summary, MRCI(Q) and FSOCI(Q) agree well with FCI when a modest basis set is used and within chemical accuracy for larger basis sets; MRCI(Q) agrees well with FSOCI(Q) when a larger basis set is used. MRCI(Q) is chosen to be the benchmark method for cases for which FCI calculations cannot be done, because MRCI(Q) is computationally much less expensive than both FCI and FSOCI(Q).

B. Comparison of ROCCL, UCCSD(T) and MRMP2. Figures 2–9 show the RCCSD, ROCCL, UCCSD(T), and MRMP2 error curves relative to MRCI(Q) for the eight bond-breaking reactions $\text{H}_2\text{A}-\text{B} \rightarrow \text{H}_2\text{A} + \text{B}$ (A is C or Si; B is H,

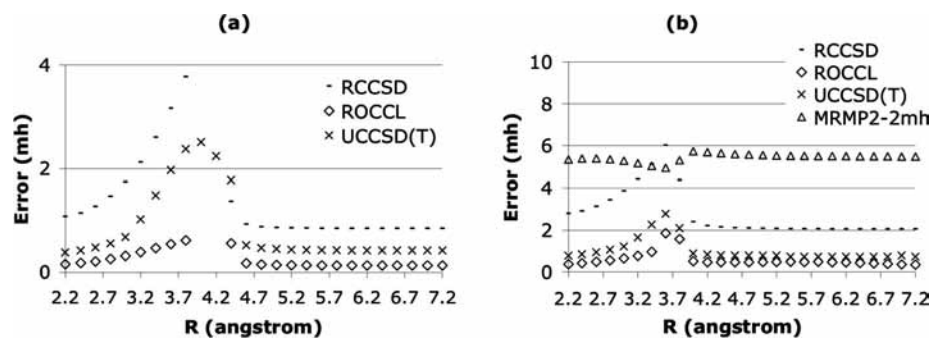


Figure 9. RCCSD, ROCCL, UCCSD(T), and MRMP2 errors relative to MRCI(Q) for $\text{H}_2\text{Si}-\text{SiH}_3 \rightarrow {}^1\text{SiH}_2 + \text{SiH}_3$. Basis sets: (a) MINI; (b) 6-31G.

TABLE 4: ROCCL/cc-pVDZ and ROCCL/cc-pVTZ* NPE, STD and REE Relative to the ROCCL/cc-pVTZ PES (mhartree Units)^a

species	NPE		STD		REE	
	ROCCL/cc-pVDZ	ROCCL/cc-pVTZ*	ROCCL/cc-pVDZ	ROCCL/cc-pVTZ*	ROCCL/cc-pVDZ	ROCCL/cc-pVTZ*
$\text{H}_2\text{C}-\text{H}$	10.459	3.908	3.291	1.227	-7.957	0.823
$\text{H}_2\text{C}-\text{Cl}$	12.825	7.604	4.148	2.271	-9.709	2.347
$\text{H}_2\text{C}-\text{CH}_3$	6.947	5.093	2.246	1.746	-4.909	-0.898
$\text{H}_2\text{C}-\text{SiH}_3$	11.281	4.581	3.922	1.645	-10.105	-3.844
$\text{H}_2\text{Si}-\text{H}$	4.960	1.155	1.754	0.314	-4.279	-0.560
$\text{H}_2\text{Si}-\text{Cl}$	13.236	4.407	4.272	1.329	-11.679	1.088
$\text{H}_2\text{Si}-\text{CH}_3$	7.489	2.072	2.198	0.476	-5.725	-0.958
$\text{H}_2\text{Si}-\text{SiH}_3$	7.660	1.665	2.202	0.417	-6.379	-0.998
unsigned average	9.357	3.811	3.004	1.178	7.593	1.440

^a The NPE, STD, and REE in the $\text{H}_2\text{C}-\text{SiH}_3$ row exclude the energy errors in the $R(\text{H}_2\text{C}-\text{SiH}_3) > 5.0 \text{ \AA}$ region due to the MP2 convergence problems.

Cl, CH_3 , or SiH_3 .) H_2A is the ground state of ${}^3\text{CH}_2$ or ${}^1\text{SiH}_2$. The RCCSD error curves all have much larger NPE than ROCCL, UCCSD(T), and MRMP2, because RCCSD does not recover nondynamic correlation energy (as MRMP2 does) and does not account for triple excitations (as ROCCL and UCCSD(T) do). Table 3 lists the corresponding NPE, STD, and REE values extracted from Figures 2–9. The STD errors are generally ~ 20 – 30% of the corresponding NPE except that the STD error is 65% of the NPE for the ROCCL/MINI PES of the $\text{H}_2\text{C}-\text{CH}_3$ bond-breaking reaction.

Figure 2 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 energy error curves for $\text{H}_2\text{C}-\text{H} \rightarrow {}^3\text{CH}_2 + \text{H}$. The emphasis here will be on the error curves obtained with double- ζ or larger basis sets. All of the ROCCL and UCCSD(T) error curves exhibit a bell shape in Figures 2–9 with double- ζ or larger basis sets. In Figures 2b–e, the ROCCL maximum errors occur at 0.4 \AA longer distances than the corresponding UCCSD(T) ones. This indicates that ROCCL remains accurate at longer bond distances than UCCSD(T) does; the same pattern is exhibited in Figures 3–9. The MRMP2 errors in Figures 2b–e decrease monotonically in the $R = 1.0$ – 2.5 \AA region before leveling off. Both the ROCCL and the UCCSD(T) NPE values are 1–2 mhartree smaller than the corresponding MRMP2 values with the cc-pVD(T)Z basis set. The ROCCL and UCCSD(T) REE values are less than 0.2 mhartree with double- ζ or larger basis sets, whereas the MRMP2 REE magnitudes are much larger, in the 1.5–5.3 mhartree range.

Figure 3 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 errors for $\text{H}_2\text{C}-\text{Cl} \rightarrow {}^3\text{CH}_2 + \text{Cl}$. The ROCCL maximum errors occur 0.2–0.4 \AA later than the UCCSD(T) errors. The MRMP2 error curves all have a shallow well with a minimum at $R \approx 3 \text{ \AA}$. The ROCCL and UCCSD(T) NPE are similar, and both are larger than the corresponding MRMP2 values by 1.5–3.7 mhartree. The ROCCL and UCCSD(T) REE

are ≤ 0.9 and 1.2 mhartree (i.e., $\leq 1 \text{ kcal/mol}$), respectively; both are 1–2 mhartree smaller than the MRMP2 REE values.

Figure 4 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 energy error curves for $\text{H}_2\text{C}-\text{CH}_3 \rightarrow {}^3\text{CH}_2 + \text{CH}_3$. The ROCCL/6-31G maximum error occurs at 0.4 \AA longer than the corresponding UCCSD(T) curve. The ROCCL [UCCSD(T)] NPE is 1.9 [2.8] mhartree larger than the corresponding MRMP2 NPE with the 6-31G basis, whereas the ROCCL [UCCSD(T)] REE is 0.6 [0.7] mhartree smaller than that for MRMP2.

Figure 5 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 error curves for $\text{H}_2\text{C}-\text{SiH}_3 \rightarrow {}^3\text{CH}_2 + \text{SiH}_3$. The maximum in the ROCCL error curve occurs at a 0.4 \AA longer distance than the UCCSD(T) curve with the 6-31G basis set. The MRMP2 error decreases in the $R = 1.8$ – 3.4 \AA regions before it levels off. The ROCCL [UCCSD(T)] NPE is 1.1 [1.6] mhartree larger than that of MRMP2/6-31G. The ROCCL [UCCSD(T)] REE value, however, is 1.1 [1.0] mhartree smaller than the corresponding MRMP2 value. All of these errors are $\sim 1 \text{ kcal/mol}$ or less.

Figure 6 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 errors for $\text{H}_2\text{Si}-\text{H} \rightarrow {}^1\text{SiH}_2 + \text{H}$. There is an apparent discontinuity in the region $R \approx 2.8$ – 3.0 \AA on the RCCSD error curves. This is because the ROHF reference changes from the reactant side determinant with a Si–H σ bond and an unpaired electron on Si to the product side determinant with a pair of lone pair electrons on Si and an unpaired electron on H. The ROCCL and UCCSD(T) energy error curves do not have such apparent discontinuities because of the inclusion of the noniterative triples corrections. In addition, both the restricted CR-CC(2,3) and unrestricted CCSD(T) approaches, ROCCL and UCCSD(T), respectively, include some degree of multireference character via the suitable treatment of higher-order correlation effects. The ROCCL NPE is smaller than that of UCCSD(T) by 0.2–1.0 mhartree and smaller than that of MRMP2 by

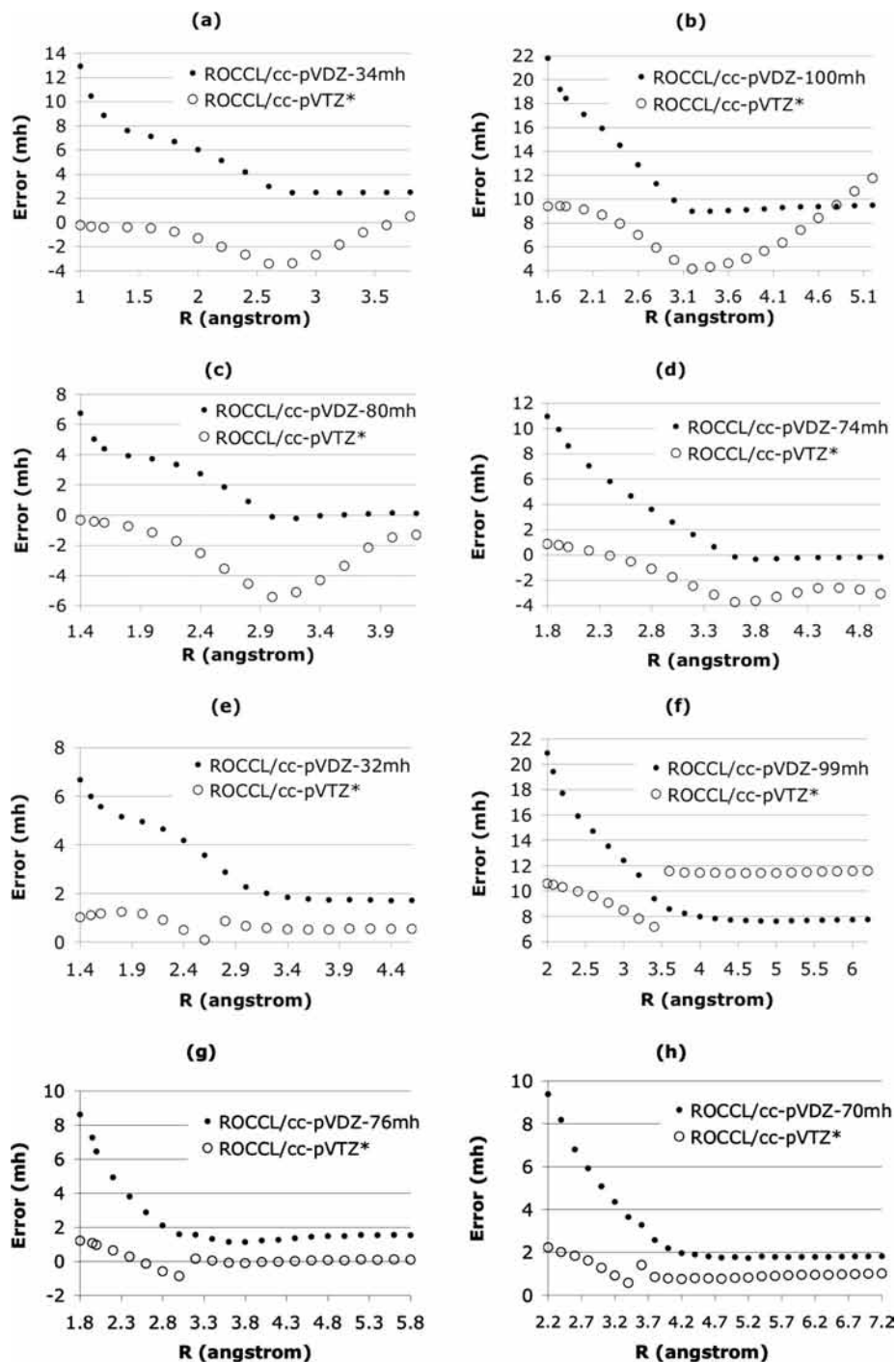


Figure 10. ROCCL/cc-pVDZ and ROCCL/cc-pVTZ* errors relative to the ROCCL/cc-pVTZ PES. Open shell species: (a) $\text{H}_2\text{C}-\text{H}$; (b) $\text{H}_2\text{C}-\text{Cl}$; (c) $\text{H}_2\text{C}-\text{CH}_3$; (d) $\text{H}_2\text{C}-\text{SiH}_3$; (e) $\text{H}_2\text{Si}-\text{H}$; (f) $\text{H}_2\text{Si}-\text{Cl}$; (g) $\text{H}_2\text{Si}-\text{CH}_3$; (h) $\text{H}_2\text{Si}-\text{SiH}_3$.

0.2–2.2 mhartree, depending on the basis set. The ROCCL and UCCSD(T) REE amplitudes are all within 0.6 mhartree regardless of the basis set; both are smaller than the corresponding MRMP2 values by 0.1–0.6 mhartree.

Figure 7 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 error curves for $\text{H}_2\text{Si}-\text{Cl} \rightarrow {}^1\text{SiH}_2 + \text{Cl}$. Here again there is a discontinuity on the RCCSD curve for the same reason as noted above. The ROCCL NPE is smaller than that of UCCSD(T) by 0.6–1.8 mhartree; it is also smaller than that of MRMP2 by 1.2–2.3 mhartree with a double- ζ or larger basis set. The ROCCL [UCCSD(T)] REE values are ≤ 1.0 [0.5] mhartree for all basis sets; the MRMP2 REE values are in the 1.8–2.9 mhartree range with double- ζ or larger basis sets.

Figure 8 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 error curves for $\text{H}_2\text{Si}-\text{CH}_3 \rightarrow {}^1\text{SiH}_2 + \text{CH}_3$. The RCCSD discontinuity again appears in the $R = 3.2\text{--}3.4$ Å region. The ROCCL/6-31G NPE is smaller than that of UCCSD(T)/6-31G by 0.3 mhartree, and 0.9 mhartree smaller than that of MRMP2/6-31G. The ROCCL and UCCSD(T) REE values are 0.1 mhartree or smaller regardless of the basis set, whereas the MRMP2/6-31G REE value is larger than 0.7 mhartree, but still within “chemical accuracy” of ~ 1 kcal/mol.⁵³

Figure 9 shows the RCCSD, ROCCL, UCCSD(T), and MRMP2 error curves for $\text{H}_2\text{Si}-\text{SiH}_3 \rightarrow {}^1\text{SiH}_2 + \text{SiH}_3$. The RCCSD discontinuity appears in the $R = 3.6\text{--}4.0$ Å region. The ROCCL NPE is 0.5 mhartree smaller than that of

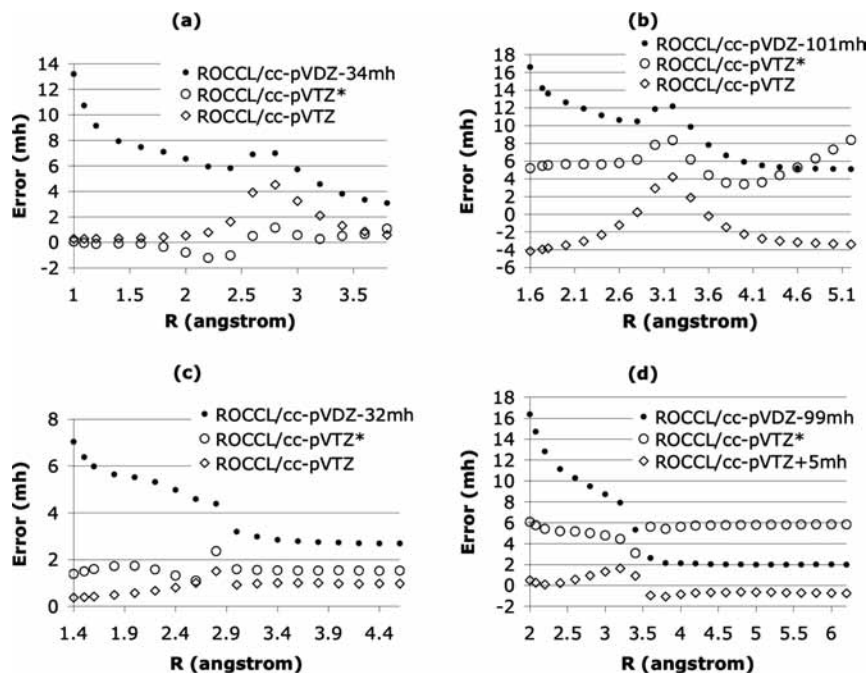


Figure 11. ROCCL/cc-pVDZ, ROCCL/cc-pVTZ*, and ROCCL/cc-pVTZ errors relative to the MRCI(Q)/cc-pVTZ PES. Open shell species: (a) $\text{H}_2\text{C}-\text{H}$; (b) $\text{H}_2\text{C}-\text{Cl}$; (c) $\text{H}_2\text{Si}-\text{H}$; (d) $\text{H}_2\text{Si}-\text{Cl}$.

TABLE 5: ROCCL/cc-pVDZ, ROCCL/cc-pVTZ*, and ROCCL/cc-pVTZ NPE, STD, and REE Relative to the MRCI(Q)/cc-pVTZ PES (mhartree Units)^a

species	ROCCL NPE			ROCCL STD			ROCCL REE		
	cc-pVDZ	cc-pVTZ*	cc-pVTZ	cc-pVDZ	cc-pVTZ*	cc-pVTZ	cc-pVDZ	cc-pVTZ*	cc-pVTZ
$\text{H}_2\text{C}-\text{H}$	10.109	2.366	4.256	2.663	0.684	1.393	-7.650	1.130	0.307
$\text{H}_2\text{C}-\text{Cl}$	11.523	4.981	8.367	3.670	1.457	2.398	-9.127	2.929	0.582
$\text{H}_2\text{Si}-\text{H}$	4.356	1.269	1.132	1.521	0.246	0.295	-3.695	0.024	0.584
$\text{H}_2\text{Si}-\text{Cl}$	14.370	2.982	2.705	4.799	0.647	0.801	-12.692	0.075	-1.013
unsigned average	10.090	2.900	4.115	3.163	0.759	1.222	8.291	1.040	0.622

^a The NPE, STD, and REE in the $\text{H}_2\text{C}-\text{H}$ row exclude the energy error at $R(\text{H}_2\text{C}-\text{H}) = 4.0 \text{ \AA}$ due to the MP2 convergence problems.

UCCSD(T) and it is 0.7 mhartree larger than that of MRMP2 with the 6-31G basis set. The ROCCL, UCCSD(T), and MRMP2 REE are 0.1 mhartree or smaller. So, again all of these errors are within ~ 1 kcal/mol.

To summarize, the ROCCL NPE are smaller than the corresponding UCCSD(T) values for seven of the eight reactions studied here, the exception being $\text{H}_2\text{C}-\text{Cl}$. ROCCL outperforms MRMP2 in the NPE for $\text{H}_2\text{C}-\text{H}$, $\text{H}_2\text{Si}-\text{H}$, $\text{H}_2\text{Si}-\text{Cl}$, and $\text{H}_2\text{Si}-\text{CH}_3$; the opposite is true for $\text{H}_2\text{C}-\text{Cl}$, $\text{H}_2\text{C}-\text{CH}_3$, $\text{H}_2\text{C}-\text{SiH}_3$, and $\text{H}_2\text{Si}-\text{SiH}_3$. Both ROCCL and UCCSD(T) are more accurate than MRMP2 in the REE for all of the eight reactions studied here. Averages of the ROCCL, UCCSD(T), and MRMP2 NPE and REE are also listed in Table 3. 6-31G is the largest basis set with which all of the eight bond-breaking reactions have been examined. The ROCCL NPE average with the 6-31G basis is 0.4 mhartree smaller than that of UCCSD(T) but 0.5 mhartree larger than that of MRMP2; the ROCCL REE unsigned average is 0.1 and 0.7 mhartree smaller than those of UCCSD(T) and MRMP2, respectively. The cc-pVTZ basis is the largest basis set used in this paper, only for the four bond-breaking reactions of $\text{H}_2\text{C}(\text{Si})-\text{H}(\text{Cl})$ due to the large computer time cost. The ROCCL NPE average with this basis set is 0.3 and 0.4 mhartree less than that of UCCSD(T) and MRMP2, respectively; the ROCCL REE unsigned average is 0.1 mhartree larger than that of UCCSD(T) and 2.2 mhartree smaller than that of MRMP2.

Table 3 and Figures 2–9 also show that ROCCL, as well as UCCSD(T) and MRMP2, differs more from MRCI(Q) with a larger basis set; this is because the larger the number of external molecular orbitals, the greater the impact of the approximations inherent in ROCCL, UCCSD(T), and MRMP2 relative to FCI. The same is true for MRCI(Q); however, the difference between MRCI(Q) and FCI is negligible, as shown in Tables 1 and 2.

C. Estimate of the ROCCL/cc-pVTZ Energies. Although ROCCL is in better agreement with MRCI(Q) with smaller basis sets, neither MRCI(Q) nor ROCCL with a small basis set can predict sufficiently accurate PESs. Generally, it is difficult to achieve adequate accuracy with smaller than triple- ζ basis sets.⁵⁴ ROCCL/cc-pVTZ was shown in the previous subsection to be capable of predicting reasonably accurate PESs for the bond-breaking reactions of open-shell species in comparison with MRCI(Q)/cc-pVTZ. However, the ROCCL computation time scales as $O(n_o^2 n_u^4)$ in the CCSD step and $O(n_o^3 n_u^4)$ in the noniterative triples step, where n_o and n_u are the numbers of occupied and unoccupied molecular orbitals, respectively. Therefore, ROCCL/cc-pVTZ calculations are computationally expensive for any but the smallest molecules. The following scheme is proposed to efficiently estimate the ROCCL/cc-pVTZ energies by assuming the additivity of basis set improvements and correlation corrections:^{53,55–63}

$$E_{\text{ROCCL/cc-pVTZ}^*} \approx E_{\text{ROCCL/cc-pVDZ}} + (E_{\text{MP2/cc-pVTZ}} - E_{\text{MP2/cc-pVDZ}}) \quad (4)$$

Such additivity relationships have been employed in many schemes. Indeed, such relationships are the foundation of the well-known and well-accepted G2 and G3 methods.^{53,55–63}

Figure 10 shows the ROCCL/cc-pVDZ and ROCCL/cc-pVTZ* energy errors relative to ROCCL/cc-pVTZ. The eight ROCCL/cc-pVDZ error curves exhibit the same pattern: the error decreases in the $R = 1-2R_e$ region before it levels off in the $R = 2-3R_e$ region. The ROCCL/cc-pVTZ* error curves are much more parallel to the horizontal axis than the ROCCL/cc-pVDZ ones, indicating a more consistently accurate level of theory. Table 4 shows that the ROCCL/cc-pVTZ* NPEs are significantly smaller than the corresponding ROCCL/cc-pVDZ NPE values. Nonetheless, the ROCCL/cc-pVTZ* NPE values relative to ROCCL/cc-pVTZ are still more than 5 mhartree for $\text{H}_2\text{C}-\text{Cl}$ and $\text{H}_2\text{C}-\text{CH}_3$; the ROCCL/cc-pVTZ* REE amplitudes are more than 2 mhartree for $\text{H}_2\text{C}-\text{Cl}$ and $\text{H}_2\text{C}-\text{SiH}_3$. However, the combination of the deviation of ROCCL/cc-pVTZ* from ROCCL/cc-pVTZ plus the deviation of ROCCL/cc-pVTZ from MRCI(Q)/cc-pVTZ is not intolerable, as discussed in the next paragraph.

Figure 11 compares the ROCCL/cc-pVDZ, ROCCL/cc-pVTZ*, and ROCCL/cc-pVTZ errors relative to MRCI(Q)/cc-pVTZ for $\text{H}_2\text{C}(\text{Si})-\text{H}(\text{Cl})$. The ROCCL/cc-pVTZ* and ROCCL/cc-pVTZ error curves are comparable to each other in parallelity and both are dramatically better than those of ROCCL/cc-pVDZ. Table 5 shows that the ROCCL/cc-pVTZ* average NPE is 1.2 mhartree smaller than that of ROCCL/cc-pVTZ compared with MRCI(Q) as the baseline, and that the unsigned average of the ROCCL/cc-pVTZ* REE is only 0.4 mhartree larger than that of ROCCL/cc-pVTZ, again relative to MRCI(Q). Therefore, ROCCL/cc-pVTZ* is demonstrated to be as accurate as the exact ROCCL/cc-pVTZ. Even so, the additivity approximation must be carefully evaluated before it can be applied to the bond-breaking reactions of open-shell species with different bond types than those studied in this work.

IV. Conclusions

It has been shown that the ROCCL method provides a viable approach to bond breaking in radicals for a broad variety of chemical reactions. Indeed, it has been demonstrated that ROCCL is a better choice than both UCCSD(T) and MRMP2 for breaking the $\text{H}_2\text{A}-\text{B}$ bonds (A is C or Si; B is H, Cl, CH_3 , or SiH_3) because the ROCCL NPE is notably smaller than that obtained from UCCSD(T) and the ROCCL REE is as accurate as the UCCSD(T) value. Also, ROCCL is comparable with MRMP2 for the NPE and much better than MRMP2 for the REE. These findings are especially significant, because the use of unrestricted methods for exploring potential energy surfaces of radicals are frequently plagued with inconsistent spin contamination that can lead to serious errors in relative energies, whereas the broad success of the single reference ROCCL approach avoids the pitfalls that one can encounter (such as intruder state problems) when using multireference perturbation theory methods.

The average ROCCL NPE (REE) is 4.1 (0.6) mhartree relative to MRCI(Q) with the cc-pVTZ basis set. ROCCL reproduces MRCI(Q) reaction energies with only an ~ 0.4 kcal/mol error, well below the 1 kcal/mol “chemical accuracy”. Small ROCCL NPE and REE suggest that the reaction rate constants and equilibrium constants needed to clarify the silicon carbide chemical vapor deposition mechanism can be reliably obtained

with the ROCCL PESs. Moreover, the ROCCL energy error bumps appear at more stretched bond distances than those obtained with UCCSD(T), demonstrating that ROCCL is more reliable than UCCSD(T) for predicting the relative energies of structures with partly stretched bonds.

Finally, ROCCL/cc-pVTZ energies can be estimated using an additivity approximation of basis set effects and correlation corrections. The estimated ROCCL/cc-pVTZ* PESs are found to be as accurate as the exact ROCCL/cc-pVTZ ones for the $\text{H}_2\text{C}(\text{Si})-\text{H}(\text{Cl})$ bond-breaking reactions, but the estimated scheme has much lower computer time cost.

Acknowledgment. This work was supported by the U.S. Department of Energy (Grant Nos. DE-FC07-05ID14661 (M.S.G.) administered by the Ames Laboratory, and DE-FG02-01ER15228 (P.P.)) and by the National Science Foundation’s Graduate Research Fellowship (J.R.G.).

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