A comparative assessment of the perturbative and renormalized coupled cluster theories with a noniterative treatment of triple excitations for thermochemical kinetics, including a study of basis set and core correlation effects

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The CCSD, CCSD(T), and CR-CC(2,3) coupled cluster methods, combined with five triple-zeta basis sets, namely, MG3S, aug-cc-pVTZ, aug-cc-pV(T+d)Z, aug-cc-pCVTZ, and aug-cc-pCV(T+d)Z, are tested against the DBH24 database of diverse reaction barrier heights. The calculations confirm that the inclusion of connected triple excitations is essential to achieving high accuracy for thermochemical kinetics. They show that various noniterative ways of incorporating connected triple excitations in coupled cluster theory, including the CCSD(T) approach, the full CR-CC(2,3) method, and approximate variants of CR-CC(2,3) similar to the triples corrections of the CCSD(2) approaches, are all about equally accurate for describing the effects of connected triply excited clusters in studies of activation barriers. The effect of freezing core electrons on the results of the CCSD, CCSD(T), and CR-CC(2,3) calculations for barrier heights is also examined. It is demonstrated that to include core correlation most reliably, a basis set including functions that correlate the core and that can treat core-valence correlation is required. On the other hand, the frozen-core approximation using valence-optimized basis sets that lead to relatively small computational costs of CCSD(T) and CR-CC(2,3) calculations can achieve almost as high accuracy as the analogous fully correlated calculations. © *2008 American Institute of Physics.*
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I. INTRODUCTION

Coupled cluster theory[1] has become a standard method for highly accurate molecular electronic structure calculations. The popularity of coupled cluster theory for accurate calculations is primarily associated with the success of the CCSD(T) (Ref. 2) method, which includes singly and doubly excited clusters by solving the CCSD (coupled cluster singles and doubles)[3] equations and connected triply excited clusters through a noniterative quasiperturbative correction added to the CCSD energy (CCSD already includes the disconnected triply excited clusters). CCSD(T) provides a size-extensive, well-balanced, and highly accurate description of many-electron correlation effects for systems dominated by dynamical correlation, and computational costs are manageable for small and moderate-sized systems because of the noniterative nature of the triples treatment. The popularity of the CCSD(T) method is also related to the fact that it is an easy-to-use single-reference approach. However, CCSD(T) can fail dramatically for describing systems involving larger nondynamical correlation effects, which arise when electronic near degeneracy[4] is present.[5–8] At least for the situations involving single bond stretching or breaking, and reaction pathways involving biradicals, this problem is remedied or ameliorated to a large extent by one of the renormalized CCSD(T) methods,[5–8] including the recently developed rigorously size extensive variant of the completely renormalized CCSD(T) theory, termed CR-CC(2,3).[6]

The CR-CC(2,3) method has so far been tested mainly for systems with even numbers of electrons,[6,7] where near degeneracy occurs in biradicals and dissociating (or very stretched) bonds. The recent extension of the CR-CC(2,3) approach to systems with odd numbers of electrons[8] has en-

abled treating near degeneracy cases more broadly, and the present article provides the first systematic comparison of the performance of CR-CC(2,3) and CCSD(T) for a diverse collection of reaction barrier heights. A few different variants of the CR-CC(2,3) theory are examined, including the full CR-CC(2,3) approach developed in Ref. 6 and three approximate variants of CR-CC(2,3) which are obtained by dropping terms in the full CR-CC(2,3) energy formula.[6,8] Two of these variants are practically identical to the triples corrections of the CCSD(2) theories developed in Refs. 9 and 10, giving us an opportunity to systematically examine the consistency among a larger variety of the noniterative triples coupled cluster methods in the context of the activation barrier calculations.

Testing coupled cluster methods for calculating barrier heights against large databases, such as Database/3 (Ref. 11) and NHTBH38/04,[12] is very time consuming. To more efficiently assess the performance of theoretical methods, we developed a smaller representative benchmark suite for thermochemical kinetics, called DBH24.[13] This representative benchmark suite statistically represents the full data set of all the forward and reverse barrier heights of the hydrogen transfer reactions (22 reactions) in Database/3 and the diverse reactions in NHTBH38/04 (19 reactions). It consists of four types of reactions, namely, hydrogen transfer (HT), heavy-atom transfer (HAT), nucleophilic substitution (NS), and unimolecular and association (UA) reactions. There are three reactions (six barrier heights because forward and reverse reactions are considered) for each type of reaction in the DBH24 database. The six barrier heights of each reaction type are denoted as HATBH6, NSBH6, UABH6, and HTBH6, respectively. This representative benchmark suite has been used to test over 200 methods (combinations of theory levels and basis sets).[13] The theory levels tested in the earlier work included single-level wave function methods, such as Hartree-Fock theory, Møller-Plesset perturbation theory, the quadratic configuration interaction approach, and coupled cluster theory; they also included multicoefficient correlation methods, local and hybrid density functional theory, and semiempirical molecular orbital methods.

In this paper, we focus on testing the CCSD, CCSD(T), and CR-CC(2,3) approaches, including four different variants of the CR-CC(2,3) theory, using all of the reactions included in the DBH24 database and five different basis sets of the triple-zeta quality with and without a frozen-core approximation. One of the main objectives of the present work is to determine if the recently developed CR-CC(2,3) methodology, which eliminates failures of CCSD(T) in the biradical and bond breaking situations, is as effective as the CCSD(T) approach in studies of barrier heights, where CCSD(T) is usually successful. If this turns out to be true, the CR-CC(2,3) approach can serve as a potentially significant improvement over CCSD(T), since it is very useful to have a theory that preserves the characteristics of CCSD(T) when CCSD(T) works and that can overcome the deficiencies of CCSD(T) when CCSD(T) breaks down. Moreover, by comparing the results of the frozen-core and all-electron calculations, we examine how effective the frozen-core approximation is in calculations of barrier heights. The effect of

freezing the core on the results of coupled cluster calculations for a diverse set of barrier heights included in the DBH24 database has not been systematically studied before. In particular, we analyze the importance of additional basis functions that correlate core electrons and that can treat core-valence correlation effects in coupled-cluster calculations.

We examine the performance of the variety of coupled cluster methods in which connected triple excitations are included noniteratively to see if different ways of handling the corrections due to connected triply excited clusters lead to a consistent description of a diverse set of reaction barrier heights. We focus on coupled cluster methods of the CCSD(T) and CR-CC(2,3)/CCSD(2) type, since higher-level coupled cluster approaches, such as CCSDT,[14] and methods including connected quadruply excited clusters have much larger computer costs that limit their applicability to small few-electron systems. Indeed, full CCSDT calculations involve expensive iterative steps that scale as $n_o^3 n_u^5$, where n_o and n_u are the numbers of occupied and unoccupied orbitals, respectively, that are used in post-self-consistent-field calculations. The least expensive corrections due to connected quadruples have steps that scale as $n_o^4 n_u^5$, $n_o^2 n_u^5$, or n_u^6 (see, e.g., Refs. 5, 9, and 10, and references therein for more details), which are prohibitive in applications where larger numbers of electrons and larger basis sets are employed. For comparison, the CCSD(T) and CR-CC(2,3) methods, and the related connected triples corrections of the CCSD(2) type have relatively inexpensive steps that scale as $n_o^2 n_u^4$ in the iterative CCSD part and $n_o^3 n_u^4$ in the noniterative triples part. In consequence, the CCSD(T) and CR-CC(2,3) approaches can be routinely applied to systems with up to about 80–100 correlated electrons and hundreds of basis functions. Because of these various practical considerations, it is important to examine the relative performance of the CCSD(T) and CR-CC(2,3) methods and the effect of freezing core electrons on the quality of barrier heights predicted by the CCSD(T) and CR-CC(2,3) calculations, as is done in the present study.

II. COMPUTATIONAL DETAILS

In the present work we systematically assessed the performance of the most practical coupled cluster methods, including the CCSD, CCSD(T), and CR-CC(2,3) approaches, with five triple-zeta basis sets by either correlating all electrons or using the frozen-core[15] approximation. The CCSD and CCSD(T) methods have been in wide use for about two decades and are, therefore, well established. The details of the more recent CR-CC(2,3) theory can be found elsewhere as well.[6,8] Here, we only mention that in analogy to the conventional CCSD(T) approach, in the CR-CC(2,3) calculations we add a correction due to triply excited clusters to the CCSD energy. The difference between CCSD(T) and CR-CC(2,3) lies in the definition of the connected triples correction, which in the CR-CC(2,3) case uses the complete form of the triply excited moments of the CCSD equations (projections of the CCSD equations on triply excited determinants) rather than the leading contributions to these moments used in CCSD(T). Moreover, in the CR-CC(2,3) approach, one renormalizes the connected triples correction through the

use of the left eigenstate of the similarity-transformed Hamiltonian of coupled cluster theory, which adds the necessary flexibility in handling the biradical and bond breaking regions of molecular potential energy surfaces.

The CR-CC(2,3) triples correction is defined, in particular, through the diagonal matrix elements $\langle\Phi_{ijk}^{abc}|\bar{H}^{CCSD}|\Phi_{ijk}^{abc}\rangle$, which enter the relevant perturbative energy denominator. Here, $\bar{H}^{CCSD}=e^{-T_1-T_2}He^{T_1+T_2}$ is the similarity-transformed Hamiltonian of CCSD, with T_1 and T_2 representing the CCSD singly and doubly excited cluster operators, and $|\Phi_{ijk}^{abc}\rangle$ are the triply excited determinants.[6,8] The full CR-CC(2,3) method, in which no terms in $\langle\Phi_{ijk}^{abc}|\bar{H}^{CCSD}|\Phi_{ijk}^{abc}\rangle$ are neglected, is referred to as variant D of CR-CC(2,3), labeled as CR-CC(2,3),D. By dropping the three-body contributions in $\langle\Phi_{ijk}^{abc}|\bar{H}^{CCSD}|\Phi_{ijk}^{abc}\rangle$ (i.e., by retaining one- and two-body contributions only), we obtain variant C of CR-CC(2,3), designated as CR-CC(2,3),C. By retaining only the one-body contributions to $\langle\Phi_{ijk}^{abc}|\bar{H}^{CCSD}|\Phi_{ijk}^{abc}\rangle$, we obtain variant B, labeled as CR-CC(2,3),B. Finally, by replacing the one-body terms in $\langle\Phi_{ijk}^{abc}|\bar{H}^{CCSD}|\Phi_{ijk}^{abc}\rangle$ by the usual orbital energy differences $(\varepsilon_a+\varepsilon_b+\varepsilon_c-\varepsilon_i-\varepsilon_j-\varepsilon_k)$, while neglecting other many-body terms in $\langle\Phi_{ijk}^{abc}|\bar{H}^{CCSD}|\Phi_{ijk}^{abc}\rangle$, we obtain variant A, designated as CR-CC(2,3),A.

Variants A and B of the CR-CC(2,3) approach are closely related to the triples parts of the CCSD(2) corrections developed by Hirata et al.[9] (variant A) and Head-Gordon and co-workers[10] (variant B), as discussed in detail in Refs. 6 and 8. In particular, the CR-CC(2,3),A method is equivalent to the CCSD(2)$_T$ approach of Hirata et al.,[9] when canonical Hartree-Fock orbitals are used. The CR-CC(2,3),B approach is equivalent, up to small details, to the triples correction of the CCSD(2) method developed by Head-Gordon and co-workers.[10] As explained in Refs. 6 and 8, the computer cost of each type of CR-CC(2,3) calculations is approximately twice the cost of the conventional CCSD(T) calculations.

All calculations in this study are based on reactant, product, and transition structures optimized at the QCISD/MG3 level with the spin-restricted formalism for closed-shell systems and the fully spin-unrestricted formalism for open-shell systems. All of our experiences to date indicate that these geometries are well suited for the present study, although we plan to examine the effect of the geometries optimized at higher levels of theory on the quality of coupled cluster results reported in this work in the future study. The main purpose of the present study is to assess the reliability of various coupled cluster approaches, basis sets, and the frozen-core approximation when one uses the QCISD/MG3 geometries. The effect of spin-orbit coupling was added to the energies of the Cl and OH radicals, which lower their energies by 0.84 and 0.20 kcal/mol, respectively.

The CCSD(T) calculations were performed using the MOLPRO 2002.6 package.[16] Spin-restricted Hartree-Fock calculations were used to obtain the reference orbitals with spin-unrestricted correlation calculations for open-shell systems and spin-restricted correlation calculations for closed-shell systems. The CR-CC(2,3),A-D calculations were carried out with the recently developed closed-shell[6] and open-shell[8] CR-CC(2,3) codes, which use the same choices as in MOLPRO for spin restriction and unrestriction and which have been incorporated in GAMESS.[17] The underlying CCSD calculations were performed with both MOLPRO and GAMESS. In the case of GAMESS, the relevant CCSD routines were described in Ref. 18, for the closed-shell case, and Ref. 8, for the open-shell case.

The five basis sets used in this work are MG3S (Ref. 19) and four correlation-consistent basis sets, namely, aug-cc-pVTZ,[20,21] aug-cc-pV(T+d)Z,[22] aug-cc-pCVTZ,[20,23] and aug-cc-pCV(T+d)Z. Note that MG3S is identical to 6-311+G($3d2f,2df,2p$) for H-Si and is similar to 6-311 +($3d2f$), but improved[24] for P-Ar. The aug-cc-pV(T+d)Z basis set is the same as aug-cc-pVTZ except that it has a single extra d function for the second row atoms from Al through Ar, and the other d functions of aug-cc-pVTZ are also optimized for these atoms. In this work, we generate the aug-cc-pCV(T+d)Z basis set which is the same as aug-cc-pCVTZ basis set except that all valence d functions are taken from aug-cc-pV(T+d)Z plus two d functions describing inner shells are taken from aug-cc-pCVTZ. The sizes of the various basis sets are indicated in Table I.

First we carried out calculations with all electrons correlated; these will be denoted as "full." The MG3S, aug-cc-pVTZ, aug-cc-pCVTZ, and aug-cc-pCV(T+d)Z basis sets were used in the full calculations. The MG3S and aug-cc-pVTZ basis sets are valence optimized, but we used them in full calculations to test the combination of full calculation and valence-optimized basis set.

We also performed calculations that account only for valence correlation. These are sometimes called "frozen core," but here we denote them just by omitting "full." The MG3S, aug-cc-pVTZ, and aug-cc-pV(T+d)Z basis set were used in frozen-core calculations.

Some of the above basis set choices are geared toward systematically assessing how significant the effect of freezing the core is on the activation barriers included in the DBH24 database. They also allow us to examine if using smaller triple-zeta basis sets of the MG3S quality leads to acceptable accuracies and consistent results at various levels of coupled cluster theory.

III. RESULTS AND DISCUSSIONS

The entire set of reaction barrier heights for the DBH24 database, as calculated with the CCSD, CCSD(T), and CR-CC(2,3),A-D approaches, combined with five triple-zeta basis sets, MG3S, aug-cc-pVTZ, aug-cc-pV(T+d)Z, aug-cc-pCVTZ, and aug-cc-pCV(T+d)Z, are given in Ref. 25. The calculated mean signed errors (MSEs) and mean unsigned errors (MUEs) of these methods are listed in Tables II–IV.

With all five basis sets, the CCSD method overestimates all the reaction barrier heights except for the forward barrier height of reaction HCN→HNC with the aug-cc-pVTZ basis set. The mean unsigned errors of the CCSD method are around or above 2.0 kcal/mol for the DBH24 database. Especially for heavy-atom transfer reactions, the CCSD method gives quite large errors (above 2.9 kcal/mol), which is much

TABLE I. The numbers of primitive and contracted basis functions for the 12 transition states studied in this work. $((M)[N]$ denotes M primitive functions and N contracted functions. Furthermore, A is shorthand for aug-cc-p in the names of the augmented correlation consistent basis sets.)

	Basis set				
Transition state	MG3S	AVTZ	AV(T+d)Z	ACVTZ	ACV(T+d)Z
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$	(249)[169]	(316)[215]	(328)[225]	(390)[278]	(402)[288]
$CH_3 + FCl \rightarrow CH_3F + Cl$	(219)[149]	(299)[211]	(305)[216]	(357)[262]	(363)[267]
$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	(219)[149]	(299)[211]	(305)[216]	(357)[262]	(363)[267]
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	(200)[138]	(309)[230]	(309)[230]	(351)[269]	(351)[269]
$H + C_2H_4 \rightarrow CH_3CH_2$	(159)[113]	(269)[207]	(269)[207]	(297)[233]	(297)[233]
$OH + CH_4 \rightarrow CH_3 + H_2O$	(159)[113]	(269)[207]	(269)[207]	(297)[233]	(297)[233]
$H + N_2O \rightarrow OH + N_2$	(167)[111]	(228)[161]	(228)[161]	(270)[200]	(270)[200]
$H + H_2S \rightarrow H_2 + HS$	(115)[81]	(165)[119]	(171)[124]	(195)[144]	(201)[149]
$H + N_2 \rightarrow HN_2$	(115)[77]	(161)[115]	(161)[115]	(189)[141]	(189)[141]
$HCN \rightarrow HNC$	(115)[77]	(161)[115]	(161)[115]	(189)[141]	(189)[141]
$H + ClH \rightarrow HCl + H$	(104)[72]	(138)[96]	(144)[101]	(168)[121]	(174)[126]
$H + OH \rightarrow O + H_2$	(74)[52]	(121)[92]	(121)[92]	(135)[105]	(135)[105]
Average	(158)[108]	(228)[165]	(231)[167]	(266)[199]	(269)[202]

worse than many density functionals with either polarized double-zeta or polarized triple-zeta basis sets.[12]

The CCSD(T) and CR-CC(2,3),A-D methods improve the results dramatically by including connected triple excitations, especially in conjunction with augmented correlation-consistent basis sets. In general, there is a great degree of consistency among the CCSD(T) and CR-CC(2,3),A-D data which suggests that the remaining relatively small errors are, most likely, due to higher-than-triply excited clusters and the finite nature of the basis sets employed in this work. In particular, previous studies show that the CR-CC(2,3),D approach faithfully reproduces the full CCSDT data (Ref. 6), so that it is unlikely that the iterative treatment of triples through the full CCSDT method alone would significantly reduce the errors. The mean unsigned errors of CCSD(T) with the MG3S basis set are about 0.9–1.0 kcal/mol both when correlating all electrons and when correlating only valence electrons, whereas the mean unsigned errors characterizing the CCSD(T) results for the augmented correlation-consistent basis sets vary between 0.4 and 0.6 kcal/mol. Comparison of Tables II and III shows that fully correlated CCSD(T) and CR-CC(2,3) calculations generally give

TABLE II. Mean signed error (MSE) and mean unsigned error (MUE) of coupled cluster methods calculated with all electrons correlated against DBH24 database (in kcal/mol).

	HATBH6		NSBH6		UABH6		HTBH6		DBH24
Method	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE
				MG3S					
CCSD(full)	4.36	4.36	2.29	2.29	1.76	1.76	2.55	2.55	2.74
CCSD(T)(full)	0.92	1.24	−0.01	0.74	0.70	0.70	0.93	1.04	0.93
CR-CC(2,3), A(full)	1.50	1.61	0.27	0.54	0.93	0.93	1.13	1.14	1.06
CR-CC(2,3), B(full)	1.72	1.77	0.47	0.57	0.96	0.96	1.19	1.19	1.12
CR-CC(2,3), C(full)	1.16	1.35	0.10	0.59	0.82	0.82	0.98	1.04	0.95
CR-CC(2,3), D(full)	1.17	1.35	0.10	0.60	0.82	0.82	0.98	1.04	0.95
				aug-cc-pVTZ					
CCSD(full)	2.85	2.85	1.83	1.83	1.28	1.28	1.06	1.06	1.76
CCSD(T)(full)	−0.72	0.84	−0.52	0.64	0.17	0.34	−0.72	0.72	0.64
				aug-cc-pCVTZ					
CCSD(full)	3.61	3.61	2.12	2.12	1.13	1.13	1.75	1.75	2.15
CCSD(T)(full)	−0.03	0.61	−0.26	0.46	0.01	0.28	−0.05	0.45	0.45
CR-CC(2,3), A(full)	0.55	0.84	0.04	0.34	0.23	0.38	0.14	0.54	0.52
CR-CC(2,3), B(full)	0.77	0.97	0.23	0.34	0.26	0.41	0.22	0.56	0.57
CR-CC(2,3), C(full)	0.42	0.76	−0.22	0.63	0.22	0.43	0.11	0.55	0.59
CR-CC(2,3), D(full)	0.42	0.76	−0.22	0.62	0.22	0.43	0.11	0.55	0.59
				aug-cc-pCV(T+d)Z					
CCSD(full)	3.60	3.60	2.15	2.15	1.13	1.13	1.76	1.76	2.16
CCSD(T)(full)	−0.05	0.58	−0.24	0.44	0.01	0.28	−0.05	0.45	0.44

TABLE III. Mean signed error (MSE) and mean unsigned error (MUE) of coupled cluster methods calculated with frozen-core approximation against DBH24 database (in kcal/mol).

| Method | HATBH6 | | NSBH6 | | UABH6 | | HTBH6 | | DBH24 |
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE
				MG3S					
CCSD	4.43	4.43	2.03	2.03	1.58	1.58	2.62	2.62	2.67
CCSD(T)	1.06	1.37	−0.25	0.94	0.53	0.53	1.04	1.10	0.98
CR-CC(2,3), A	1.63	1.76	0.03	0.75	0.76	0.76	1.23	1.23	1.12
CR-CC(2,3), B	1.85	1.91	0.22	0.63	0.80	0.80	1.29	1.29	1.16
CR-CC(2,3), C	1.28	1.49	−0.17	0.83	0.66	0.66	1.08	1.10	1.02
CR-CC(2,3), D	1.29	1.49	−0.18	0.83	0.65	0.65	1.08	1.10	1.02
				aug-cc-pVTZ					
CCSD	3.54	3.54	1.66	1.66	1.03	1.11	1.72	1.72	2.01
CCSD(T)	0.01	0.91	−0.67	0.68	−0.06	0.40	−0.04	0.57	0.64
CR-CC(2,3), A	0.58	1.20	−0.39	0.44	0.17	0.47	0.15	0.62	0.68
CR-CC(2,3), B	0.80	1.32	−0.20	0.35	0.19	0.49	0.23	0.65	0.70
CR-CC(2,3), C	0.46	1.13	−0.70	0.77	0.16	0.48	0.11	0.64	0.75
CR-CC(2,3), D	0.46	1.13	−0.71	0.77	0.15	0.48	0.11	0.64	0.75
				aug-cc-pV(T+d)Z					
CCSD	3.41	3.41	1.82	1.82	1.03	1.11	1.69	1.69	2.01
CCSD(T)	−0.13	0.67	−0.53	0.62	−0.06	0.40	−0.06	0.54	0.56
CR-CC(2,3), A	0.45	0.88	−0.24	0.39	0.17	0.47	0.13	0.60	0.58
CR-CC(2,3), B	0.67	1.00	−0.05	0.30	0.19	0.49	0.20	0.63	0.61
CR-CC(2,3), C	0.30	0.80	−0.53	0.60	0.16	0.48	0.09	0.62	0.62
CR-CC(2,3), D	0.31	0.80	−0.54	0.60	0.15	0.48	0.09	0.62	0.62

TABLE IV. Mean signed error (MSE) and mean unsigned error (MUE) for 5 reactions containing S and Cl (in kcal/mol).

| Method | SClHATBH4 | | SClNSBH4 | | SClHTBH2 | | SClDBH10 |
	MSE	MUE	MSE	MUE	MSE	MUE	MUE
			aug-cc-pVTZ				
CCSD	2.77	2.77	1.28	1.28	1.77	1.77	1.97
CCSD(T)	0.02	0.91	−0.72	0.73	0.45	0.47	0.75
CR-CC(2,3), A	0.42	1.04	−0.48	0.56	0.68	0.68	0.78
CR-CC(2,3), B	0.60	1.12	−0.30	0.44	0.72	0.72	0.77
CR-CC(2,3), C	0.40	0.90	−1.10	1.10	0.69	0.69	0.94
CR-CC(2,3), D	0.40	0.90	−1.10	1.10	0.68	0.68	0.94
			aug-cc-pV(T+d)Z				
CCSD	2.57	2.57	1.51	1.51	1.71	1.71	1.98
CCSD(T)	−0.19	0.54	−0.50	0.64	0.38	0.38	0.55
CR-CC(2,3), A	0.21	0.56	−0.25	0.48	0.61	0.61	0.54
CR-CC(2,3), B	0.40	0.64	−0.08	0.35	0.66	0.66	0.53
CR-CC(2,3), C	0.16	0.41	−0.85	0.85	0.62	0.62	0.63
CR-CC(2,3), D	0.17	0.41	−0.84	0.84	0.62	0.62	0.63
			aug-cc-pCVTZ				
CCSD(full)	2.77	2.77	1.75	1.75	1.63	1.63	2.13
CCSD(T)(full)	−0.12	0.51	−0.30	0.59	0.23	0.23	0.49
CR-CC(2,3), A(full)	0.30	0.55	−0.03	0.40	0.46	0.46	0.48
CR-CC(2,3), B(full)	0.49	0.64	0.15	0.32	0.51	0.51	0.48
CR-CC(2,3), C(full)	0.25	0.40	−0.57	0.69	0.47	0.47	0.53
CR-CC(2,3), D(full)	0.25	0.40	−0.57	0.69	0.47	0.47	0.53
			aug-cc-pCV(T+d)Z				
CCSD(full)	2.75	2.75	1.80	1.80	1.64	1.64	2.15
CCSD(T)(full)	−0.14	0.46	−0.26	0.57	0.24	0.24	0.46

slightly better results than frozen-core calculations. The CCSD(T)(full)/aug-cc-pCV(T+d)Z method gives the best results among all the tested methods with a mean unsigned error of only 0.44 kcal/mol, although the overall accuracy of the CR-CC(2,3),A-D approaches is practically the same as that of CCSD(T), with only minimally higher mean unsigned errors by 0.02–0.14 kcal/mol compared to CCSD(T) when the most complete variant of CR-CC(2,3), i.e., variant D, is examined. On the other hand, for the nucleophilic substitution reactions, CR-CC(2,3) performs better than CCSD(T), improving the mean unsigned errors by about 0.1–0.3 kcal/mol with all the tested basis sets.

For the reactions containing S and Cl atoms, the additional d functions in the aug-cc-pV(T+d)Z basis sets improve the frozen-core CCSD(T) and CR-CC(2,3) results by about 0.2–0.3 kcal/mol compared with the aug-cc-pVTZ basis sets (see Table IV).[25] On the other hand, the aug-cc-pCV(T+d)Z basis sets give almost the same results as the corresponding aug-cc-pCVTZ basis sets at the all-electron CCSD(T) level.

Unlike CCSD, CCSD(T) sometimes underestimates barrier heights; in particular, of the 24 barrier heights in the DBH24 database, it underestimates seven (eight) barrier heights in frozen-core (full) calculations with MG3S basis set, 17 barrier heights in fully correlated calculations with the aug-cc-pVTZ basis sets, and 14 barrier heights with each of the other three correlation-consistent basis sets. The CR-CC(2,3) approach may also underestimate barrier heights in some cases, although not as often as CCSD(T). In particular, of the 24 barrier heights in the DBH24 database, 8 barriers obtained with the aug-cc-pCVTZ basis sets and 11 barriers obtained with each of the aug-cc-pV(T+d)Z and aug-cc-pVTZ basis sets are underestimated by the CR-CC(2,3),D calculations.

Although CCSD(T)(full)/MG3S and CR-CC(2,3)(full)/MG3S calculations occasionally improve the accuracy by about 0.05 kcal/mol as compared to frozen-core approximation, it is not recommended to use valence-optimized basis sets when including core and core-valence correlation since this is not only more expensive, but a potential source of problems.[26] Note that the MG3S basis set is much smaller than the aug-cc-pVTZ basis set, as shown in Table I, while providing high quality results. The combination of the MG3S basis set with the CCSD(T) or CR-CC(2,3) methods is a good choice to balance the accuracy and computational costs in calculations for larger systems.

The mean unsigned errors characterizing the CR-CC(2,3) results listed in Tables II and III show that variants C and D of CR-CC(2,3) give almost the same results, which indicate the negligible role of the three-body components in the $\langle \Phi_{ijk}^{abc} | \bar{H}^{\mathrm{CCSD}} | \Phi_{ijk}^{abc} \rangle$ terms defining the CR-CC(2,3) triples correction. They are also on average somewhat more accurate than the formally less complete A and B variants when the MG3S basis set is employed. Variants A and B of CR-CC(2,3) seem to be slightly more accurate than variants C and D when the correlation-consistent basis sets are employed. The CR-CC(2,3) method, particularly its most complete variant D, represents a useful alternative to CCSD(T), preserving, as shown here, the high accuracy of CCSD(T) in

barrier height calculations, while offering significant advantages over CCSD(T) in the more multireference bond breaking and biradical regions examined in the earlier work.[6–8]

IV. SUMMARY AND CONCLUDING REMARKS

We have tested six practical variants of coupled cluster theory with five types of basis sets against a diverse barrier height database. Our results are consistent with the earlier studies in the literature that indicate the inclusion of connected triple excitations is essential to achieving high accuracy for thermochemical kinetics with coupled cluster theory. We have provided additional extensive evidence in this regard by showing that the CCSD(T) method and four variants of the recently developed CR-CC(2,3) theory, including two variants that are practically equivalent to the triples corrections of the CCSD(2) approaches, give very similar results for a wide variety of barrier heights in the DBH24 database. The observed consistency among various noniterative triples coupled cluster levels indicates that the elimination of the remaining small errors in the CCSD(T) and CR-CC(2,3) results would require using higher and much less practical levels of coupled cluster theory and basis sets larger than the triple-zeta basis sets tested in the present work. We have systematically examined the effect of freezing core electrons and adding additional basis functions that describe core correlations on the quality of coupled cluster results for a diverse set of activation barriers included in the DBH24 database. We have demonstrated that to include core correlation energy reliably in coupled cluster calculations, basis sets including functions that correlate the core and that can treat core-valence correlation, such as aug-cc-pCV(T+d)Z, are required. On the other hand, the frozen-core approximation can achieve high accuracy using considerably smaller valence-optimized basis sets, such as MG3S, with relatively inexpensive computational costs. Our results indicate that on average the CR-CC(2,3) theory provides activation barriers that are very similar to those obtained with the conventional CCSD(T) method, when the DBH24 database is examined. This is an encouraging finding, particularly considering the fact that the CR-CC(2,3) approach is also capable of eliminating failures of CCSD(T) in the bond breaking and biradical regions of molecular potential energy surfaces, as shown, for example, in Refs. 6–8, without making the calculations more complicated or considerably more expensive. Based on the results provided in this paper and the earlier work reported in Refs. 6–8, we can conclude that the CR-CC(2,3) approach can be regarded as an improvement over CCSD(T), since it is as accurate, on average, as CCSD(T) in calculations involving a diverse set of activation barriers constituting the DBH24 database, while overcoming the deficiencies of CCSD(T) in applications involving single bond breaking and biradicals.

[1] F. Coester, Nucl. Phys. **7**, 421 (1958); F. Coester and H. Kümmel, *ibid.* **17**, 477 (1960); J. Čížek, J. Chem. Phys. **45**, 4256 (1966); Adv. Chem. Phys. **14**, 35 (1969); J. Čížek and J. Paldus, Int. J. Quantum Chem. **5**, 359 (1971); J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A **5**, 50 (1972); J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. **14**, 545 (1978); R. J. Bartlett and G. D. Purvis, *ibid.* **14**, 561 (1978); R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989); K. Raghavachari, Annu. Rev. Phys. Chem. **42**, 615 (1991); R. J. Bartlett, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), Part I, p. 1047; K. Raghavachari and J. B. Anderson, J. Phys. Chem. **100**, 12960 (1996); J. Gauss, in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998), Vol. 1, p. 615; J. Paldus and X. Li, Adv. Chem. Phys. **110**, 1 (1999); T. D. Crawford and H. F. Schaefer III, Rev. Comput. Chem. **14**, 33 (2000); J. Paldus, in *Handbook of Molecular Physics and Quantum Chemistry*, edited by S. Wilson (Wiley, Chichester, 2003), Vol. 2, p. 272.

[2] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[3] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[4] D. R. Hartree, W. Hartree, and B. Swirles, Philos. Trans. R. Soc. London, Ser. A **238**, 229 (1939); V. McKoy and O. Sinanoglu, J. Chem. Phys. **41**, 2689 (1964); G. Das and A. C. Wahl, *ibid.* **44**, 87 (1966); J. H. Davis, W. A. Goddard, and L. B. Harding, J. Am. Chem. Soc. **99**, 2919 (1977); P. Baybutt, F. W. Bobrowicz, L. R. Kahn, and D. G. Truhlar, J. Chem. Phys. **68**, 4809 (1978); M. W. Schmidt and M. S. Gordon, Annu. Rev. Phys. Chem. **49**, 233 (1998); D. G. Truhlar, J. Comput. Chem. **28**, 73 (2007).

[5] P. Piecuch and K. Kowalski, in *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczyński (World Scientific, Singapore, 2000), Vol. 5, p. 1; K. Kowalski and P. Piecuch, J. Chem. Phys. **113**, 18 (2000); P. Piecuch, K. Kowalski, I. S. O. Pimienta, and M. J. McGuire, Int. Rev. Phys. Chem. **21**, 527 (2002); P. Piecuch, K. Kowalski, I. S. O. Pimienta, P.-D. Fan, M. Lodriguito, M. J. McGuire, S. A. Kucharski, T. Kuś, and M. Musial, Theor. Chem. Acc. **112**, 349 (2004).

[6] P. Piecuch and M. Włoch, J. Chem. Phys. **123**, 224105 (2005); P. Piecuch, M. Włoch, J. R. Gour, and A. Kinal, Chem. Phys. Lett. **418**, 467 (2006); M. Włoch, M. D. Lodriguito, P. Piecuch, and J. R. Gour, Mol. Phys. **104**, 2149 (2006).

[7] C. J. Cramer, M. Włoch, P. Piecuch, C. Puzzarini, and L. Gagliardi, J. Phys. Chem. A **110**, 1991 (2006); C. J. Cramer, A. Kinal, M. Włoch, P. Piecuch, and L. Gagliardi, *ibid.* **110**, 11557 (2006); A. Kinal and P. Piecuch, *ibid.* **111**, 734 (2007); P. Piecuch, M. Włoch, and A. J. C. Varandas, Theor. Chem. Acc. (in press); Y. Ge, M. S. Gordon, and P. Piecuch, J. Chem. Phys. **127**, 174106 (2007).

[8] M. Włoch, J. R. Gour, and P. Piecuch, J. Phys. Chem. A **111**, 11359 (2007).

[9] S. Hirata, M. Nooijen, I. Grabowski, and R. J. Bartlett, J. Chem. Phys. **114**, 3919 (2001); **115**, 3967(E) (2001); S. Hirata, P.-D. Fan, A. A. Auer, M. Nooijen, and P. Piecuch, *ibid.* **121**, 12197 (2004).

[10] S. R. Gwaltney and M. Head-Gordon, Chem. Phys. Lett. **323**, 21 (2000); S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **113**, 3548 (2000); S. R. Gwaltney and M. Head-Gordon, *ibid.* **115**, 2014 (2001); S. R. Gwaltney, E. F. C. Byrd, T. Van Voorhis, and M. Head-Gordon, Chem. Phys. Lett. **353**, 359 (2002).

[11] B. J. Lynch and D. G. Truhlar, J. Phys. Chem. A **107**, 3898 (2003).

[12] Y. Zhao, N. Gonzalez-Garcia, and D. G. Truhlar, J. Phys. Chem. A **109**, 2012 (2005).

[13] J. Zheng, Y. Zhao, and D. G. Truhlar, J. Chem. Theory Comput. **3**, 569 (2007).

[14] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987); **89**, 3401(E) (1988); G. E. Scuseria and H. F. Schaefer III, Chem. Phys. Lett. **152**, 382 (1988).

[15] E. S. Sachs, J. Hinze, and N. H. Sabelli, J. Chem. Phys. **62**, 3393 (1975).

[16] H.-J. Werner, P. J. Knowles, R. D. Amos *et al.*, MOLPRO, University of Birmingham, Birmingham, 2002.

[17] M. W. Schmidt, K. K. Baldridge, J. A. Boatz *et al.*, J. Comput. Chem **14**, 1347 (1993); M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry: the First Forty Years*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005), p. 1167 (the open-shell CR-CC(2,3) method has been available in GAMESS since June 2007; release R6 of the 24 March 2007 version of GAMESS, released on Dec. 12, 2007, has added several enhancements in the code and updated references in the output).

[18] P. Piecuch, S. A. Kucharski, K. Kowalski, and M. Musiał, Comput. Phys. Commun. **149**, 71 (2002).

[19] B. J. Lynch, Y. Zhao, and D. G. Truhlar, J. Phys. Chem. A **107**, 1384 (2003).

[20] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989); D. E. Woon and T. H. Dunning, *ibid.* **98**, 1358 (1993).

[21] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[22] T. H. Dunning, K. A. Peterson, and A. K. Wilson, J. Chem. Phys. **114**, 9244 (2001).

[23] D. E. Woon and T. H. Dunning, J. Chem. Phys. **103**, 4572 (1995); K. A. Peterson and T. H. Dunning, *ibid.* **117**, 10548 (2002).

[24] L. A. Curtiss, K. Raghavachari, C. Redfern, V. Rassolov, and J. A. Pople, J. Chem. Phys. **109**, 7764 (1998).

[25] See EPAPS Document No. E-JCPSA6-128-001803 for electronic files, in pdf format, containing tabulations of full set of calculated reaction barrier heights for the DBH24 database with CCSD, CCSD(T), and CR-CC(2,3) combined with aug-cc-pCVTZ, aug-cc-pVTZ, and MG3S basis sets. This document can be reached through a direct link in the online articles's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

[26] P. R. Taylor, in *Lecture Notes in Quantum Chemistry*, edited by B. O. Roos (Springer-Verlag, Berlin, 1992), p. 406.