Assessment of the CCSD and CCSD(T) Coupled-Cluster Methods in Calculating Heats of Formation for Zn Complexes

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Heats of formation were calculated using coupled-cluster methods for a series of zinc complexes. The calculated values were evaluated against previously conducted computational studies using density functional methods as well as experimental values. Heats of formation for nine neutral ZnX_n complexes [X = −Zn, −H, −O, $-F_2$, −S, −Cl, $-Cl_2$, $-CH_3$, $(-CH_3)_2$] were determined at the CCSD and CCSD(T) levels using the 6-31G** and TZVP basis sets as well as the LANL2DZ-6-31G** (LACVP**) and LANL2DZ-TZVP hybrid basis sets. The CCSD(T)/6-31G** level of theory was found to predict the heat of formation for the nonalkyl Zn complexes most accurately. The alkyl Zn species were problematic in that none of the methods that were tested accurately predicted the heat of formation for these complexes. In instances where experimental geometric parameters were available, these were most accurately predicted by the CCSD/6-31G** level of theory; going to CCSD(T) did not improve agreement with the experimental values. Coupled-cluster methods did not offer a systemic improvement over DFT calculations for a given functional/basis set combination. With the exceptions of ZnH and ZnF_2, there are multiple density functionals that outperform coupled-cluster calculations with the 6-31G** basis set.

Introduction

Zinc complexes are critically important in biological systems, serving in both a structural and a catalytic capacity.[1,2] Indeed, zinc trails only iron as the most ubiquitous transition metal in biological systems. Key complexes include but are certainly not limited to human carbonic anhydrase,[3−5] carboxypeptidase,[6] alcohol dehydrogenase,[7] and so-called "zinc fingers",[8,9] which play structural roles in DNA recognition. Many of these systems have been studied extensively via X-ray crystallography and spectroscopic methods, including NMR.

The literature to date contains many computational studies on systems that contain zinc. In a 1991 study, Kaupp et al. probed the structures of ZnR_2 complexes with 1,4-diaza-1,3-butadienes using pseudopotential calculations.[10] A subsequent study by Kaupp and von Schnering probed the structures and binding energies of $(ZnX_2)_2$ dimers at the MP2 and HF levels of theory using pseudopotentials.[11] Kabelac and Hobza examined the binding of Zn^{2+} with the nucleic acid bases adenine, guanine, cytosine, and thymine at the MP2/TZVP level of theory.[12] In recent work, Rayon and coworkers have probed binding energies and geometries of several Zn^{II} complexes using MP2 and density functional methods for optimizations along with single-point calculations at the CCSD(T)/aug-cc-pVTZ level of theory.[13]

We have recently employed a variety of popular density functional methods spanning the GGA, meta-GGA, hybrid-GGA, and meta-hybrid-GGA functional classes, a total of 12, in the calculation of both heat of formation (ΔH_f) and ionization potential for transition-metal complexes.[14] This study utilized both the Pople-style 6-31G** and the TZVP basis sets. Further efforts within the group have applied the same set of density functionals in conjunction with the pseudopotential-based LANL2DZ[15] basis set on Zn.

Although not as abundant as work with lower-level methods, some literature precedent for the application of coupled-cluster methods to ΔH_f calculations in small organic systems does exist. Dixon and coworkers have investigated iodine fluorides using CCSD(T) methods[16] and applied similar methodology in the study of diazomethane.[17] Feller and Franz used large basis-set-coupled cluster calculations to determine ΔH_f values for furan and other related derivatives.[18] Related work by Feller and coworkers includes the determination of ΔH_f values for combustion products,[19] oxyfluorides,[20] and borohydrides.[21] Harding and coworkers evaluated the ΔH_f value of vinyl chloride using high-level ab initio calculations under the HEAT protocol with geometries optimized at the CCSD(T) level.[22] Marenich and Boggs performed CCSD(T) calculations to investigate formyl and isoformyl radical species.[23] Additionally, Lee has studied compounds of the form $XONO_2$ (X = H, F, Cl) using coupled-cluster methods and determined a heat of formation value for $FONO_2$ using isodesmic reactions.[24] Martin and coworkers have probed thermodynamic properties of bromoalkanes[25] and boron trifluoride,[26] including investigation of relativistic effects.

There is also some precedent for the use of these methods in ΔH_f calculations on metal-containing systems. A popular approach is extrapolation toward the complete basis set (CBS) limit and has been applied to transition-metal compounds from Sc−Zn.[27,28] Further work by DeYonker et. al describes the application of the correlation-consistent composite approach to the thermochemistry of transition-metal systems.[29] Sullivan et al. used CCSD(T) calculations to determine ΔH_f values for oxide and hydroxide complexes of alkali and alkaline earth metals.[30] Similarly, Nielsen and coworkers used CCSD(T) calculations in the study of tin−oxygen compounds.[31] Finally, Lu and coworkers have recently published high-level calculations on transition-metal−ammonia complexes at the CCSD(T) level extrapolated to the CBS limit to predict ionization potentials

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TABLE 1: Experimental and Best DFT ΔH_f Values for Zn Complexes

			best density functional calculation[a]			
	experimental[33]		6-31G**		TZVP	
entry	ΔH_f	error	ΔH_f	method	ΔH_f	method
Zn_2	57.7	1.5	57.37	BLYP	62.77	PBEPBE
ZnH	62.9	0.5	57.96	B98	63.34	PBE1PBE
ZnO	52.8	0.9	52.06	BB1K	52.89	MPWPW91
ZnF_2	–118.9	1.1	–130.06	BB1K	–118.59	TPSSKCIS
ZnS	48.7	3.0	49.95	TPSS1KCIS	62.05	BB95
ZnCl	6.5	1.0	5.14	B3LYP	8.08	TPSSTPSS
$ZnCl_2$	–63.5	0.4	–66.78	B3LYP	–62.63	TPSSTPSS
$ZnCH_3$	26.0	2.5	26.44	PBEPBE	44.47	TPSSTPSS
$Zn(CH_3)_2$	12.9	2.0	–3.59	BB1K	13.34	MPWPW91

[a] From Riley and Merz.[14]

accurately.[32] Whereas it may not be practical to apply the highly accurate CCSD(T)-CBS extrapolated model to larger transition-metal-containing systems, we desired to probe the efficacy of CCSD and CCSD(T) calculations with smaller basis sets in predicting the heats of formation of such systems because to our knowledge, this has not been examined closely. Moreover, as far as we are aware, extensive coupled-cluster calculations including full geometry optimizations have not been used in the prediction of ΔH_f values for Zn complexes.

We desired to expand our efforts toward the calculation of heat of formation values to include more powerful computational methods. Our current efforts are focused on the application of coupled-cluster methods toward this end. Higher-level calculations such as CASPT2 were not employed because these are not viable for larger Zn-containing systems, and one of our primary reasons for these investigations is the uncovering of computational methodologies suitable for use in QM- and QM/MM-type calculations on biological systems incorporating one or more Zn centers. With this in mind, we have focused on using relatively modest basis sets (e.g., 6-31G** and TZVP) combined with the CCSD (coupled-cluster with single and double excitations) and CCSD(T) (coupled-cluster with single and double and perturbative triple excitations) methods for the purpose of this study. CCSD(T) provides an excellent compromise between accuracy and computational cost, and we wish to evaluate its performance in determining ΔH_f values for ZnX_n complexes. CCSD is less computationally intensive, and we evaluate this method as well because it may be more amenable to the study of larger Zn systems. In the future, the effect of larger basis sets will be explored, but the present effort represents a balance between accuracy and computational efficacy.

We have chosen a series of zinc complexes (ZnX_n) to be the focus of our initial work with coupled cluster methods for ΔH_f calculations. The nine chosen ZnX_n complexes are Zn_2, ZnH, ZnO, ZnF_2, ZnS, ZnCl, $ZnCl_2$, $ZnCH_3$, and $Zn(CH_3)_2$, and these were selected on the basis of the availability of literature heats of formation. These compounds present a mix of both open and closed shell species, albeit with either singlet or doublet ground-state multiplicities, except in the cases of ZnS and ZnO (vide infra). Table 1 contains experimental heats of formation with errors and the calculated values using the "best" density functional method with both the 6-31G** and TZVP basis sets from the work of Riley and Merz.[14] These "best" values represent the density functional providing the smallest deviation from the reported experimental values with each respective basis set. The errors associated with the literature values for this set are relatively small, with the noted exceptions of ZnCl and $Zn(CH_3)_2$, whose errors are 15.4 and 15.5%, respectively, relative to the reported values. One can readily identify the problem with the application of DFT methods in calculations on Zn complexes; there is no "universal method" providing optimal results. It is hoped that coupled-cluster methods can systematically reduce the overall error and either provide a more global approach to calculations on Zn complexes, or at least demonstrate that the best approach to heats of formation in these complexes is the identification of a complex-specific density functional.

Computational Methodology. All calculations were carried out on a SUN cluster featuring dual 2.5 GHz Opteron nodes using the Gaussian 03[34] suite of programs. All geometry optimizations incorporated standard gradient methods. For all single-point calculations, the SCF=TIGHT keyword was used. The SCF=XQC keyword was applied in all instances because SCF convergence was often problematic, especially for higher-energy multiplets. CCSD and CCSD(T) calculations were run as implemented in Gaussian 03.[35−40] Frequency calculations were conducted on all geometries (at the minimum energy multiplicity) to ensure that all calculated lowest-energy structures resided at local minima on the potential energy surface. Where applicable, calculations were done at the UCCSD and UCCSD(T) levels. All other calculations are closed shell. The Pople type 6-31G** and triple-ζ quality TZVP basis sets were used as implemented in Gaussian 03.[41,42] LACVP** calculations were run using the GEN keyword for the basis set. In these calculations, the LANL2DZ basis/pseudopotential was used for Zn, and the 6-31G** basis set was used for the nonmetal atoms. A second set of calculations was run, which applied the TZVP basis set to the nonmetals while retaining LANL2DZ on the Zn atom. T1 diagnostics were computed with Gaussian 03 at the CCSD/6-31G** and CCSD/TZVP levels of theory.[43,44] This is a measure that identifies instances where multireference effects may be important. Whereas multireference methods are beyond the intent of this investigation, we have placed these values in the Supporting Information because the results identify several compounds for which multireference approaches should be considered (ZnO, ZnS, and ZnF_2).

For all Zn species considered, we initially desired to optimize the 1, 3, 5, and 7 multiplicities for even electron species and the 2, 4, 6, and 8 multiplicities for odd electron species, as done in our previous DFT work.[14] This worked well for most CCSD calculations, although it was sometimes difficult to achieve SCF convergence for high-energy multiplicities. CCSD(T) calculations failed for a large number of high-energy multiplicities. The low-energy multiplicities determined at the CCSD level of theory could always be submitted for successful optimization at the CCSD(T) level for the nonalkyl complexes, and hence we are confident that all of the ground states were able to be determined at both coupled-cluster levels. $Zn(CH_3)_2$ proved to have serious convergence problems in the geometry optimization procedure for the CCSD(T) calculations and uses the numerical eigenvector-following algorithm in Gaussian, and attempts at the CCSD(T) level were abandoned for this system at all multiplicities. At C_1 symmetry, the lowest for this system, $Zn(CH_3)_2$ experienced difficulties with the number of variables as well. Enforcing D_{3h} symmetry to decrease the variables considered did not provide any relief for convergence related problems.

Heats of formation (ΔH_f) for all complexes were computed using the method outlined in the Gaussian white paper on thermochemistry in the Gaussian 03 online manual.[45] These calculations follow eq 1, which simplifies to eq 2, derived from the procedures outlined in the Gaussian white paper. The "M" and "X" designations in eq 1 correspond to the molecule and

TABLE 2: CCSD and CCSD(T) ΔH_f Values for Zn Complexes; 6-31G**

		6-31G**		LACVP**[a]	
entry	ΔH_f (exp)	CCSD	CCSD(T)	CCSD	CCSD(T)
$^1Zn_2$	57.7	64.3	64.1	64.5	64.4
^2ZnH	62.9	63.7	63.8	69.9	70.1
ZnO	52.8	64.2[b]	56.0[b]	73.0[c]	71.1[b]
$^1ZnF_2$	–118.9	–119.9	–121.8	–98.3	–99.5
ZnS	48.7	75.6[b]	70.9[b]	88.0[c]	84.1[b]
^2ZnCl	6.5	13.3	12.6	23.5	22.9
$^1ZnCl_2$	–63.5	–51.7	–53.7	–32.1	–33.7
$^2ZnCH_3$	26	63.9	61.4	74.1	71.9
$^1Zn(CH_3)_2$	12.9	44.0		64.9	
average error[d,e]		–12.6	–10.1	–23.8	–22.3
rmsd[e]		12.5	11.8	13.8	12.8

[a] LANL2DZ on Zn; 6-31G** on nonmetal atoms. [b] Singlet. [c] Triplet. [d] Error calculated as ΔH_f(exptl) − ΔH_f(calcd). [e] Average error and rmsd exclude $Zn(CH_3)_2$ values for basis of comparison.

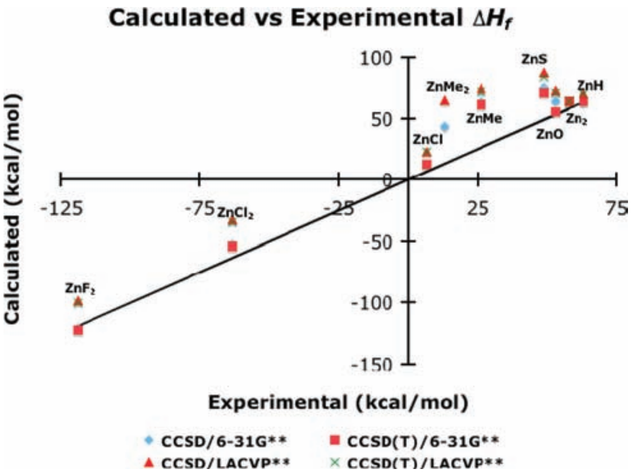

Figure 1. Calculated versus experimental ΔH_f values.

individual atoms, respectively. For convenience, eq 2 is provided in terms of the output provided by Gaussian 03.

$$\Delta H_f(\mathrm{M, 298\ K}) = \Delta H_f(\mathrm{M, 0\ K}) + ((H_\mathrm{M}(298\ \mathrm{K}) - H_\mathrm{M}(0\ \mathrm{K})) - \sum x(H_x(298\ \mathrm{K}) - H_x(0\ \mathrm{K})) \tag{1}$$

$$\Delta H_f(298\ \mathrm{K}) = 627.5095(E_\mathrm{CORR}) + 31.17 - 627.5095(E_\mathrm{Zn}) + \Delta H_f(\mathrm{atom, 298\ K}) - 627.5095(E_\mathrm{atom}) \tag{2}$$

E_CORR is identified as the sum of electronic and thermal enthalpies from the output of the Gaussian frequency calculation (which includes thermal and ZPE corrections to the energy). E_Zn and E_atom are the energies of the Zn and nonmetal atoms at a given level of theory. The constant 31.17 (kcal/mol) in eq 2 is the ΔH_f (Zn, 298 K) taken from the NIST chemistry WebBook,[46] and the respective ΔH_f (atom, 298 K) values for the nonmetals are found there as well. Finally, eq 3 was implemented in the calculation of root mean squared deviations (rmsd's).

$$\sqrt{\frac{1}{n}\sum_{i}^{n}(x_i - \bar{x})^2} \tag{3}$$

Results and Discussion

Summarized in Table 2 are calculated heats of formation for Zn complexes at the CCSD and CCSD(T) levels for all applications of the 6-31G** basis set (stand-alone and as part of LACVP**). A plot of all calculated values versus the experimental ΔH_f for an illustrative comparison is given in Figure 1. For each metal entry, most data points are grouped rather closely together. Significant deviations from the experimental values were found in calculated ΔH_f values for several of the complexes investigated. Most ZnX_n species at all levels of theory possessed a calculated ΔH_f substantially higher than the experimental value. The exceptions were $^1ZnF_2$ at both the CCSD/6-31G** and CCSD(T)/6-31G** levels of theory. These were slightly lower than the experimental value, at 1.0 and 2.9 kcal/mol, respectively. All other complexes had overestimated ΔH_f values at each method/basis set combination. ΔH_f values for diatomic $^1Zn_2$ are consistently calculated for both CCSD and CCSD(T) calculations with the 6-31G** and LACVP** basis sets; however, the errors across the board are nearly 7 kcal/mol. For ^2ZnH, the calculated values are off by nearly the same amount for both coupled cluster methods with the LACVP** basis set/pseudopotential, but with the 6-31G** basis set, the calculated heats of formation are within 1.0 kcal/mol of the experimental value, which represents excellent agreement. The ΔH_f values calculated for ^1ZnS were significantly larger than the experimental values. The percentage errors in the calculated values ranged from 45.6% at CCSD(T)/6-31G** to 80.7% at CCSD/LACVP**. Very large errors were observed in the calculated ΔH_f values for $^1ZnCl_2$ at both the CCSD/LACVP** and CCSD(T)/LACVP** levels of theory (49.4 and 46.9% errors, respectively).

The calculated ΔH_f values for $^2ZnCH_3$ were poor across all investigated levels of theory. The best calculated value was 61.4 kcal/mol at the CCSD(T) level of theory, which compared with the experimental value is 136.2% higher in energy. Both values calculated using the LACVP** basis set were significantly worse, with percentage errors approaching 200%. So whereas it may be argued that the CCSD(T)/6-31G** level of theory is the best level of theory presented for $^2ZnCH_3$, it is quite clear that none of the these combinations were really appropriate for this species. In the cases where $^1Zn(CH_3)_2$ can be evaluated, the values are again poor. A full discussion of this complex is presented elsewhere (vide infra).

Overall, calculations using the 6-31G** basis set always perform better than their LACVP** counterparts. In six of eight cases, CCSD(T)/6-31G** outperforms CCSD/6-31G** with the two exceptions being ^2ZnH (by 0.1 kcal/mol) and $^1ZnF_2$ (by 1.6 kcal/mol). CCSD(T)/LACVP** outperforms CCSD/LACVP** in all cases except for ^2ZnH. The average error associated with CCSD(T)/6-31G** is −10.1 kcal/mol, a 2.5 kcal/mol improvement over the average for CCSD/6-31G**. The average error increases nearly two-fold for both CCSD and CCSD(T) calculations using the LACVP** basis set.

Next, we will focus on the geometries of species for which experimental data are available: ^2ZnH, $^1ZnF_2$, $^1ZnCl_2$, and $^1Zn(CH_3)_2$. Table 3 contains a summary of Zn−X bond lengths for all complexes, with the aforementioned available literature values. For ^2ZnH, the Zn−H bond length is calculated to within 0.001 Å at the CCSD/6-31G** and CCSD(T)/6-31G** levels of theory. The deviation from experimental is significantly larger for both coupled-cluster methods using the LACVP** basis set: 0.057 Å for CCSD and 0.058 Å for CCSD(T). For $^1ZnF_2$, the reverse trend is observed in that coupled-cluster methods

TABLE 3: Experimental[47] and Calculated Equilibrium Zn−X Bond Distances for Zn Complexes[a]

		6-31G**		LACVP**	
entry	exptl (Zn−X)	CCSD	CCSD(T)	CCSD	CCSD(T)
^{1}Zn2		4.252	4.192	4.741	4.680
^{2}ZnH	1.594	**1.594**	1.593	1.651	1.652
ZnO		1.706	1.700	1.878	1.743
$^{1}ZnF_2$	1.742	1.709	1.709	**1.731**	**1.731**
ZnS		2.058	2.057	2.335	2.122
^{2}ZnCl		2.144	2.145	2.205	2.208
$^{1}ZnCl_2$	2.072	**2.079**	2.080	2.137	2.138
$^{2}ZnCH_3$		1.980	1.979	2.066	2.067
$^{1}Zn(CH_3)_2$	1.930	**1.928**		1.993	

[a] All values are in angstroms. Closest calculated values are in **bold** font.

TABLE 4: CCSD and CCSD(T) ΔH_f Values for Zn Complexes; TZVP

		TZVP		LANL2DZ[a]	
entry	ΔH_f (exp)	CCSD	CCSD(T)	CCSD	CCSD(T)
$^{1}Zn_2$	57.7	65.0	64.9	64.5	64.4
^{2}ZnH	62.9	66.7	66.9	67.9	68.0
ZnO	52.8	78.6[b]	69.7[c]	72.2[c]	68.1[b]
$^{1}ZnF_2$	–118.9	–101.4	–105.1	–98.8	–102.3
ZnS	48.7	83.1[c]	79.3[b]	85.4[b]	80.1[b]
^{2}ZnCl	6.5	18.1	17.4	20.3	19.5
$^{1}ZnCl_2$	–63.5	–46.6	–48.6	–38.6	–40.4
$^{2}ZnCH_3$	26	71.6	68.7	71.3	68.3
$^{1}Zn(CH_3)_2$	12.9			58.8	
average error[d,e]		–20.4	–17.6	–21.5	–19.3
rmsd[e]		13.3	12.0	13.1	11.9

[a] LANL2DZ on Zn; TZVP on nonmetal atoms. [b] Singlet. [c] Triplet. [d] Error calculated as ΔH_f(exptl) − ΔH_f(calcd). [e] Average error and rmsd exclude $Zn(CH_3)_2$ values for basis of comparison.

TABLE 5: Experimental[45] and Calculated Equilibrium Zn−X Bond Distances for Selected Zn Complexes[a]

		TZVP		LANL2DZ-TZVP	
entry	exptl (Zn−X)	CCSD	CCSD(T)	CCSD	CCSD(T)
^{1}Zn2		5.212	5.212	4.741	4.680
^{2}ZnH	1.594	1.621	**1.619**	1.637	1.636
ZnO		1.748	1.882	1.891	1.752
$^{1}ZnF_2$	1.742	**1.748**	1.751	1.751	1.754
ZnS		2.280	2.091	2.120	2.116
^{2}ZnCl		2.173	2.173	2.200	2.203
$^{1}ZnCl_2$	2.072	**2.109**	**2.109**	2.133	2.135
$^{2}ZnCH_3$		2.042	2.041	2.060	2.059
$^{1}Zn(CH_3)_2$	1.930			1.986	

[a] All values are in angstroms. Closest calculated values are in **bold** font.

incorporating the LACVP** basis set calculate Zn−F bond lengths to within 0.01 Å, whereas methods utilizing strictly the Pople-style 6-31G** basis set arrive at equilibrium bond lengths 0.033 Å lower than the experimental value. For $^{1}ZnCl_2$, CCSD/6-31G** predicts the most accurate bond length, within 0.007 Å of the experimental value (CCSD(T)/6-31G** is nearly as accurate, off by 0.008 Å). Both methods with the LACVP** basis set are off by at least 0.04 Å. Finally, the Zn−C bond distance in $^{1}Zn(CH_3)_2$ is calculated to within 0.002 Å at the CCSD/6-31G** level of theory and within 0.063 Å at CCSD/LACVP**. The Zn−X distances for which experimental data are not available are scattered at best among the levels of theory, but with no literature values available, it is difficult to assess which methods are "correct" in their predictions. Three points are immediately obvious: (1) the 6-31G** basis set is preferred over LACVP** for these heat of formation predictions, (2) there is no obvious trend with respect to over- or underestimation of bond lengths, and (3) applying the CCSD(T) level offers no significant improvement on calculated equilibrium bond lengths with a constant basis set; indeed, the geometries typically deviate more from the experimental value using the higher-level method.

To probe further the effect of the basis set on these calculations, we ran all calculations using the TZVP basis set. Calculated heats of formation for ZnX_n complexes at the CCSD and CCSD(T) levels for all applications of the TZVP basis set (stand-alone and in conjunction with LANL2DZ) are summarized in Table 4 and Figure 3. All calculated ΔH_f values were overestimated using these two basis sets. As with the 6-31G** basis sets, the two methyl Zn species had poorly predicted ΔH_f values. The $^{1}Zn_2$ and ^{2}ZnH complexes were again consistently well calculated by all methods used. As with the 6-31G** and LACVP** basis sets, the calculated ΔH_f values for ZnS were very poor, with nearly 100% errors at all four levels of theory. Large errors for ZnO were also observed in each instance. Errors in ZnS and ZnO are further discussed in the section dealing with the calculation of their ground-state spin multiplicities. The ΔH_f values for $^{1}ZnCl_2$ were best calculated at the CCSD/TZVP and CCSD(T)/TZVP levels of theory with percentage errors of 26.6 and 23.5%, respectively; clearly, the overall performance for calculations involving this dichloride was rather poor.

As was observed using the Pople-style basis set, TZVP and LANL2DZ-TZVP results for $^{2}ZnCH_3$ were quite poor. All errors well surpassed 100% of the experimental value, ranging from a low of 162.7% for CCSD(T)/LANL2DZ-TZVP to a high of 175.4% at the CCSD/TZVP level of theory. Of the eight methods utilized during the course of this study, not one does an adequate job of predicting the ΔH_f value for $^{2}ZnCH_3$.

The predicted bond lengths were compared against experimental values for ^{2}ZnH, $^{1}ZnF_2$, $^{1}ZnCl_2$, and $^{1}Zn(CH_3)_2$ (Table 5). The CCSD(T)/TZVP geometry for ^{2}ZnH was closest to the experimental r_{Zn-H}, overestimating by 0.025 Å. The CCSD/TZVP level of theory best described the Zn−F bond length in $^{1}ZnF_2$ and was off by only 0.006 Å. Both the CCSD and CCSD(T) methods in conjunction with the TZVP basis set gave a Zn−Cl bond distance of 2.109, 0.037 Å higher than the experimental r_{ZnCl} value in $^{1}ZnCl_2$. $^{1}Zn(CH_3)_2$ could be optimized only at the CCSD/LANL2DZ-TZVP level of theory, and r_{Zn-C} was overestimated by 0.056 Å. For the three complexes that could be optimized at all levels of theory incorporating TZVP or LANL2DZ-TZVP, the TZVP basis set performed better, although there was very little variation in the results for $^{1}ZnF_2$. There was no clear separation between the CCSD and CCSD(T) methods, with CCSD better for $^{1}ZnF_2$, CCSD(T) better for ^{2}ZnH (both by slim margins), and both methods producing identical geometries for $^{1}ZnCl_2$ (Figure 2).

Overall, CCSD(T)/6-31G** and CCSD(T)/TZVP calculations best predict the heat of formation for the seven nonalkyl Zn complexes. These methods are compared in Figure 3. The CCSD(T)/6-31G** level of theory is shown to outperform the CCSD(T)/TZVP level slightly in these ΔH_f predictions. The difference in average errors between these two methods is 5.0 kcal/mol, with CCSD(T)/631G** averaging a −9.0 kcal/mol deviation and CCSD(T)/TZVP differing from the experimental by an average of −14.0 kcal/mol for the seven nonalkyl complexes.

Calculated Multiplicities. In general, all levels of theory correctly predicted the appropriate spin ground states for the

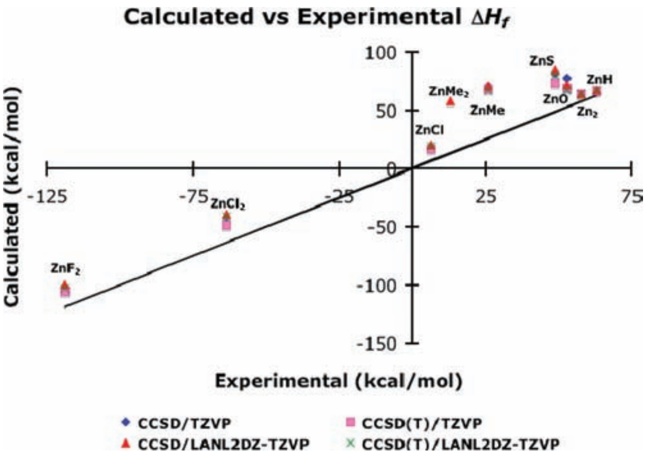

Figure 2. Calculated versus experimental ΔH_f values.

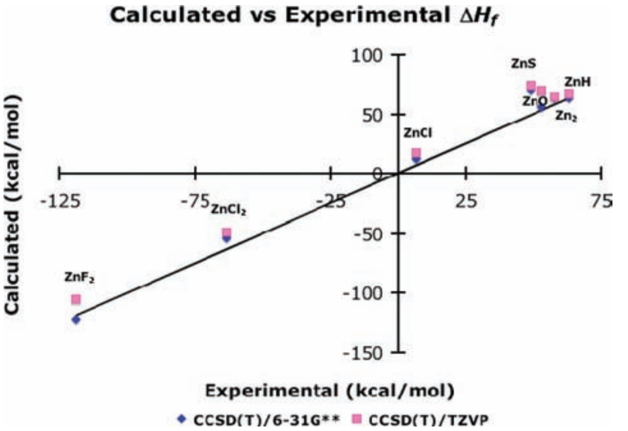

Figure 3. Comparison of CCSD(T) ΔH_f values with 6-31G** and TZVP basis sets.

Zn species investigated. Open shell species were found to be ground-state doublets, and closed shell species were found to be ground-state singlets. There are two notable exceptions, and these are the cases of ZnO and ZnS. The expected ground-state multiplicity, insofar as what species the heat of formation is determined for, is ambiguous. Experimental work indicates that the available heat of formation and Zn−X bond lengths are for the triplet.[45,48] However, the most accurate calculations to date on these complexes predict a ground-state singlet multiplicity.[49,50] The triplet ground-state was predicted for ZnO at the CCSD/LACVP**, CCSD(T)/TZVP, and CCSD/LANL2DZ-TZVP levels of theory. The triplet was found to be the ground state of ZnS at only the CCSD/LACVP** and CCSD/LANL2DZ-TZVP levels of theory. The pseudopotential incorporating basis sets with the CCSD level of coupled-cluster theory most often arrive at the triplet ground state for both ZnO and ZnS. The lowest errors in calculated ΔH_f values were observed using the TZVP and 6-31G** basis sets, which most frequently predict the singlet ground-state multiplicities. For ZnO, theoretical studies support a triplet ground state for bond lengths in excess of 1.85 Å and a singlet for distances closer to the reported internuclear distance of 1.69 Å.[48] These findings are in complete agreement with the predicted ground states in our study. Other investigations in our laboratory have turned up similar confusion in predicted ground-state spins: in our LANL2DZ investigation,[15] a singlet ground state was predicted for all GGA and meta-GGA functionals and a triplet ground state was predicted for all hybrid-GGA and hybrid-meta-GGA functionals.

TABLE 6: CCSD/6-31G ΔH_f Values with and without Second-Order DKH Relativistic Correction for Nonalkyl Zn Complexes**

		CCSD/6-31G**		CCSD/6-31G** w/DKH	
entry	ΔH_f (exp)	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]
$^1Zn_2$	57.7	64.3	–6.6	64.1	–6.4
^2ZnCl	6.5	13.3	–6.8	14.6	–8.1
$^1ZnCl_2$	–63.5	–51.7	–11.8	–50.7	–12.8
ZnO	52.8	64.2[b]	–11.4	61.8[c]	–9.0
$^1ZnF_2$	–118.9	–119.9	1.0	–119.0	0.1
ZnS	48.7	75.6[b]	–26.9	76.0[b]	–27.3
^2ZnH	62.9	63.7	–0.8	64.1	–1.2
average error			–9.0		–9.3
rmsd			8.6		8.5

[a] $\Delta\Delta H_f$ calculated as ΔH_f(exptl) – ΔH_f (calcd). [b] Singlet. [c] Triplet.

TABLE 7: CCSD(T)/6-31G ΔH_f Values with and without Second-Order DKH Relativistic Correction for Nonalkyl Zn Complexes**

		CCSD(T)/6-31G**		CCSD(T)/6-31G** w/DKH	
entry	ΔH_f (exp)	ΔH_f	$\Delta\Delta H_f$[a]	ΔH_f	$\Delta\Delta H_f$[a]
^2ZnCl	6.5	12.6	–6.1	13.9	–7.4
$^1ZnCl_2$	–63.5	–53.7	–9.8	–52.7	–10.8
ZnO	52.8	56.0[b]	–3.2	60.6[c]	–7.8
$^1ZnF_2$	–118.9	–121.8	2.9	–120.9	2.0
ZnS	48.7	70.9[b]	–22.2	71.4[b]	–22.7
^2ZnH	62.9	63.8	–0.9	64.3	–1.4
average Error			6.6		8.0
rmsd			8.0		7.8

[a] $\Delta\Delta H_f$ calculated as ΔH_f(exptl) − ΔH_f(calcd). [b] Singlet. [c] Triplet.

Relativistic Correction. We decided to further our investigation by applying a Douglas−Kroll−Hess second-order relativistic correction (DKH) to calculations at the CCSD/6-31G** level of theory, as implemented in Gaussian 03.[51−55] This correction was applied during the course of both the geometry optimizations and frequency analyses. A comparison of CCSD/6-31G** ΔH_f values with and without this correction is provided in Table 6. The addition of the DKH correction actually results in a slight increase in the average heat of formation error. The error is decreased with this correction for $^1Zn_2$, ZnO, and $^1ZnF_2$, whereas it is increased for the remaining entries. It is worthwhile to point out that not only does the addition of a second-order relativistic correction improve the calculated ΔH_f value for ZnO, it also results in the prediction of a triplet ground state for the species, as opposed to the singlet predicted by the standard CCSD/6-31G** calculation.

Table 7 contains results for CCSD(T)/6-31G** calculations including relativistic effects for six ZnX_n complexes. The alkyl Zn species were omitted, and efforts to include this correction for $^1Zn_2$ failed. The average error increases by 1.4 kcal/mol with the inclusion of this correction compared with the same set of six compounds using standard CCSD(T)/6-31G** calculations. Only the error for $^1ZnF_2$ decreases with the second-order correction, whereas all other errors increase in magnitude. The most significant increase in error is associated with ZnO. There is also a ground-state multiplicity change for this species, which is predicted to be a triplet with the inclusion of the DKH correction, whereas at the CCSD(T)/6-31G** level of theory, it is predicted to possess a ground-state singlet multiplicity.

$Zn(CH_3)_2$. There are two viable conformations for $^1Zn(CH_3)_2$, specifically, conformations that have pseudoeclipsed hydrogen atoms and pseudo-anti-hydrogen atoms (Figure 4). Both conformations were examined during the course of this study. The pseudoeclipsed conformation was found to be a minimum at

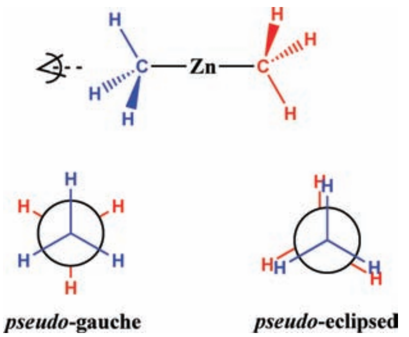

Figure 4. Newman projections depicting viable $Zn(CH_3)_2$ conformations.

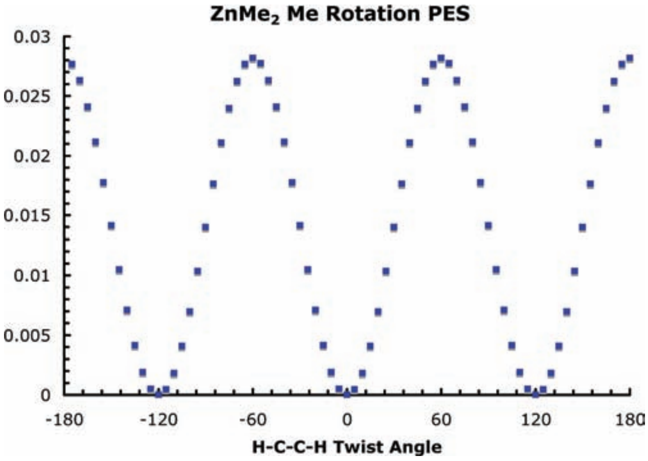

Figure 5. Relative conformational energy versus H−C−C−H twist for $^1Zn(CH_3)_2$ (CCSD/6-31G**); unrelaxed scan in 5° increments. Minima at −120, 0, and 120° correspond to the pseudoeclipsed conformation; maxima at −60, 60, and 180° correspond to pseudogauche.

both the CCSD/6-31G** and CCSD/TZVP levels of theory, whereas the pseudo-anti-conformer was calculated to be a transition state, as evidenced by the presence of one negative mode in the vibrational analysis. The energy difference between the two conformations is quite small, 0.03 kcal/mol at CCSD/6-31G**, which implies virtually no barrier to free rotation of the methyl groups because this value is lower than kT. This is not surprising because a bridging Zn atom separates these substituents. A plot of the unrelaxed potential energy surface for methyl rotation is displayed in Figure 5 (relative energy as a function of H−C−C−H twist angle).

The eclipsed conformation is perhaps favored over the gauche conformation because of stabilizing hyperconjugative interactions with the d orbitals of the bridging Zn atom and the C−H antibonding orbitals; the eclipsed conformation affords more of these interactions than does the gauche. Therefore, the potential energy surface is essentially a 60° shift of that seen in ethane (where the pseudogauche conformation is most stable and the pseudoeclipsed is a rotational transition state). We are currently investigating bulkier alkyl substituents (e.g., $ZnEt_2$ and Zn^iPr_2) to see if this trend of eclipsed conformational preference continues. Unfortunately, the size of these species will preclude any investigations using higher level methods such as CCSD(T), but we are confident that density functional methods and CCSD calculations will prove to be adequate in these efforts.

Density Functional Theory Comparison. Finally, we compare the CCSD/6-31G** and CCSD(T)/6-31G** results to those obtained using density functional theory with the same basis set in previous work.[14] Table 8 offers a side-by-side comparison of the coupled cluster and DFT results. Coupled-cluster calculations outperformed all listed density functionals for ZnH and ZnF_2 by a significant margin. These were the only two species for which at least one density functional did not outperform both coupled-cluster data sets. In most cases, for the remaining entries, multiple density functionals could be identified, providing better results than their coupled-cluster counterparts. So, whereas the CCSD and CCSD(T) values can be said to be clearly superior to DFT for the halide and difluoride, the systemic improvement desired for the overall data set is not there. Indeed, if one calculates the average errors for a given data set, coupled cluster methods run in the middle of the pack when compared with the twelve listed density functionals with the 6-31G** basis set. Given the added computational cost associated with coupled-cluster methods, it is sensible to take the time to select carefully a density functional that give the best results with respect to predicting thermodynamic properties such as the heat of formation in Zn complexes for routine application studies.

Conclusions

For nine ZnX_n complexes, ΔH_f values were calculated using the CCSD and CCSD(T) coupled cluster methods in conjunction with the 6-31G**, TZVP, LANL2DZ-6-31G** (LACVP**), and LANL2DZ-TZVP basis sets. In general, the 6-31G** basis set was found to outperform the other three, and the CCSD(T)/6-31G** level of theory provided ΔH_f values that compared most favorably to the experimental values, slightly outperform-

TABLE 8: CCSD/6-31G, CCSD(T)/6-31G**, and DFT (6-31G**) $\Delta\Delta H_f$ Values (Experimental − Calculated)[a]**

	$\Delta\Delta H_f$								
method	Zn_2	ZnH	ZnO	ZnF_2	ZnS	ZnCl	$ZnCl_2$	$ZnCH_3$	$Zn(CH_3)_2$
BLYP	0.33	8.51	24.12	27.45	–3.31	1.45	3.39	–10.76	19.69
MPWPW91	2.56	10.12	27.27	34.09	2.66	8.45	14.24	–2.75	33.08
PBEPBE	3.00	9.46	28.86	35.88	3.84	8.84	16.44	–0.44	38.80
B3LYP	–3.13	7.96	7.37	16.45	–8.79	1.36	3.28	–11.00	20.71
PBE1PBE	–1.93	8.38	7.15	18.34	–4.79	7.64	12.77	–7.36	26.12
B98	–2.59	4.94	7.65	18.54	–4.86	2.01	9.75	–13.15	20.09
TPSSTPSS	2.95	15.76	23.68	33.75	4.25	10.99	17.98	2.34	41.92
TPSSKCIS	1.92	32.73	25.03	32.73	3.51	9.44	15.31	–1.41	34.49
BB95	1.35	8.79	30.21	36.29	4.52	7.09	14.29	–4.83	31.72
B1B95	–3.58	7.42	5.10	18.30	–4.60	6.00	11.41	–10.94	20.67
TPSS1KCIS	–0.99	11.12	13.30	23.41	–1.25	8.23	12.94	–4.47	29.36
BB1K	–4.87	7.22	0.74	11.16	–8.37	6.08	10.85	–13.09	16.49
CCSD	**–6.57**	**–0.79**	**–11.41**	**1.02**	**–26.88**	**–6.83**	**–11.78**	**–37.94**	**–31.13**
CCSD(T)	**–6.43**	**–0.94**	**–3.22**	**2.90**	**–22.20**	**–6.10**	**–9.84**	**–35.44**	

[a] This work is in **bold**. All DFT numbers are from ref 14 and the supporting information therein.

ing CCSD(T)/TZVP calculations. For the four complexes for which experimental equilibrium bond lengths were available, the CCSD/6-31G** level of theory generally provided the best geometries, with CCSD(T)/6-31G** bond lengths actually deviating more from the experimental distances in most cases. The lone exception to this trend was $^1ZnF_2$, for which the CCSD/TZVP level of theory predicted the most accurate r_{Zn-F} value. CCSD(T) calculations could not be performed on $^1Zn(CH_3)_2$ because of the size of the system, and CCSD calculations on this system provided poor heat of formation values. All levels of theory resulted in poor predicted heats of formation for $^2ZnCH_3$.

In general, CCSD/6-31G** calculations seem to be appropriate for the prediction of heat of formation values for nonalkylated species, with the CCSD(T) method providing slight improvement. On the basis of the previous work, it may be more time efficient to select carefully the appropriate density functional for a given system as the system size increases because coupled-cluster methods do not offer a systemic improvement over their DFT counterparts.[14,15] The CCSD/6-31G** level of theory does a good job of reproducing the experimental bond distances in these systems. The addition of a second-order Douglas−Kroll−Hess relativistic correction does not provide overall improvement in the calculated ΔH_f values. Rather, this term offers modest improvement in some instances while actually resulting in an increased error for other entries. The fact that CCSD values are comparable to CCSD(T) values is important because this method is clearly more amenable to calculations on larger systems, whereas the CCSD(T) calculations would quickly become too resource-intensive to be viable. We are currently extending our research to include complexes of other 3d transition metals to determine the extent of applicability of coupled-cluster methods to these systems.

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Supporting Information Available: T1 diagnostics computed at the CCSD/6-31G** and CCSD/TZVP levels of theory and spreadsheets detailing all heat of formation calculations at all investigated levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239.

(2) Lipscomb, W. N.; Strater, N. *Chem. Rev.* **1996**, *96*, 2375.

(3) Kannan, K. K.; Notstrand, B.; Fridborg, K.; Lövgren, S.; Ohlsson, A.; Petef, M. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 51.

(4) Liljas, A.; Kannan, K. K.; Bergstén, P.-C.; Waara, I.; Fridborg, K.; Strandberg, B.; Carlbom, U.; Järup, L.; Lövgren, S.; Petef, M. *Nature New Biol.* **1972**, *235*, 131.

(5) Eriksson, A. E.; Jones, T. A.; Liljas, A. *Proteins* **1988**, *4*, 274.

(6) Dideberg, O.; Charlier, P.; Dive, G.; Joris, B.; Frere, J. M.; Ghuysen, J. M. *Nature* **1982**, *299*, 469.

(7) Eklund, H.; Nordstrom, B.; Zeppezauer, E.; Soderlund, G.; Ohlsson, I.; Boiwe, T.; Soderberg, B.-O.; Tapia, O.; Branden, C.-I.; Åkeson, Å. *J. Mol. Biol.* **1976**, *102*, 27.

(8) Klug, A.; Schwabe, J. W. R. *FASEB J.* **1995**, *9*, 597.

(9) Berg, J. M.; Shi, Y. *Science* **1996**, *271*, 1081.

(10) Kaupp, M.; Stoll, H.; Preuss, H.; Kaim, W.; Stahl, T.; van Koten, G.; Wissing, E.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5606.

(11) Kaupp, M.; von Schnering, H. G. *Inorg. Chem.* **1994**, *33*, 4718.

(12) Kabelac, M.; Hobza, P. *J. Phys. Chem. B* **2006**, *110*, 14515.

(13) Rayon, V. M.; Valdes, H.; Diaz, N.; Suarez, D. *J. Chem. Theory. Comput.* **2008**, *4*, 243.

(14) Riley, K. E.; Merz, K. M. *J. Phys. Chem. A* **2007**, *111*, 6044.

(15) Yang, Y.; Weaver, M. N.; Riley, K. E.; Merz, K. M. Assessment of the 6-31+G**/LANL2DZ basis set coupled with density functional theory methods: prediction of heats of formation and ionization potentials for third row transition metal complexes *J. Phys. Chem. A* **2008**, submitted for publication.

(16) Dixon, D. A.; Grant, D. J.; Christe, K. O.; Peterson, K. A. *Inorg. Chem.* **2008**, *47*, 5485.

(17) Dixon, D. A.; de Jong, W. A.; Peterson, K. A.; McMahon, T. B. *J. Phys. Chem. A* **2005**, *109*, 4073.

(18) Feller, D.; Franz, J. A. *J. Phys. Chem. A* **2000**, *104*, 9017.

(19) Feller, D.; Dixon, D. A.; Francisco, J. S. *J. Phys. Chem. A* **2003**, *107*, 1604.

(20) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 9641.

(21) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053.

(22) Harding, M. E.; Gauss, J.; Pfluger, K.; Werner, H.-J. *J. Phys. Chem. A* **2007**, *111*, 13623.

(23) Marenich, A. V.; Boggs, J. E. *J. Phys. Chem. A* **2003**, *107*, 2343.

(24) Lee, T. J. *J. Phys. Chem.* **1995**, *99*, 1943.

(25) Oren, M.; Iron, M. A.; Burcat, A.; Martin, J. M. L. *J. Phys. Chem. A* **2004**, *108*, 7752.

(26) Bauschlicher, C. W., Jr.; Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem. A* **1999**, *103*, 7715.

(27) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107.

(28) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2006**, *125*, 074110.

(29) DeYonker, N. J.; Peterson, K. A.; Steyl, G.; Wilson, A. K.; Cundari, T. R. *J. Phys. Chem. A* **2007**, *111*, 11269.

(30) Sullivan, M. B.; Iron, M. A.; Redfern, P. C.; Martin, J. M. L.; Curtiss, L. A.; Radom, L. *J. Phys. Chem. A* **2003**, *107*, 5617.

(31) Nielsen, I. M. B.; Janssen, C. L.; Allendorf, M. D. *J. Phys. Chem. A* **2003**, *107*, 5122.

(32) Li, S.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *128*, 154301.

(33) *Thermal Constants of Substances*; Yungman, V. S., Ed.; Wiley: New York, 1999; Vol. 4−6.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(35) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(36) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(37) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382.

(38) Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700.

(39) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(40) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.

(41) For references describing the standard abbreviations and basic ab initio methods, see the following: (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. (b) Clark, T. *A Handbook of Computational Chemistry*; Wiley-Interscience: New York, 1985.

(42) Schafer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(43) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.* **1989**, *S23*, 199–207.

(44) Korth, M.; Grimme, S. *J. Chem. Theory Comput.* **2009**, *5*, 993.

(45) The Gaussian white paper dealing with thermochemistry is available on the web at the following URL: http://www.gaussian.com/g_whitepap/thermo.htm.

(46) The NIST chemistry WebBook is accessible at the following URL: http://webbook.nist.gov/chemistry/.

(47) Bredow, T.; Geudtner, G.; Jug, K. *J. Comput. Chem.* **2001**, *22*, 861.

(48) Clemmer, D. E.; Dalleska, N. F.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *95*, 7263.

(49) Peterson, K. A.; Shepler, B. C.; Singleton, J. M. *Mol. Phys.* **2007**, *105*, 1139.

(50) Boughdiri, S.; Tangour, B.; Teichteil, C.; Barthelat, J.-C.; Leininger, T. *Chem. Phys. Lett.* **2008**, *462*, 18.

(51) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.

(52) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756.

(53) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742.

(54) Jansen, G.; Hess, B. A. *Phys. Rev. A* **1989**, *39*, 6016.

(55) deJong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

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