

Calculation of Heats of Formation for Zn Complexes: Comparison of Density Functional Theory, Second Order Perturbation Theory, Coupled-Cluster and Complete Active Space Methods

Michael N. Weaver,[†] Kenneth M. Merz, Jr.,^{*,†,‡} Dongxia Ma,[§] Hyun Jung Kim,[§] and Laura Gagliardi^{*,§}

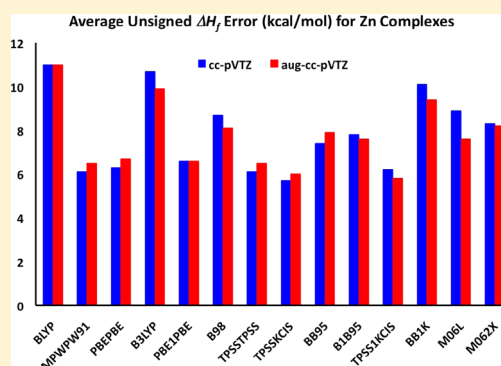
[†]Department of Chemistry Quantum Theory Project, University of Florida, 2328 New Physics Building, Gainesville, Florida 32611-8435, United States

[‡]Department of Chemistry Department of Biochemistry and Molecular Biology, Michigan State University, 578 S. Shaw Lane, East Lansing, Michigan 48824-1322, United States

[§]Department of Chemistry Supercomputing Institute and Chemical Theory Center, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0431, United States

S Supporting Information

ABSTRACT: Heats of formation were predicted for nine ZnX complexes (X = Zn, H, O, F₂, S, Cl, Cl₂, CH₃, (CH₃)₂) using 14 density functionals, MP2 calculations, and the CCSD and CCSD(T) coupled-cluster methods. Calculations utilized the correlation consistent cc-pVTZ and aug-cc-pVTZ basis sets. Heats of formation were most accurately predicted by the TPSSSTPSS and TPSSKCISS density functionals, and the BLYP, B3LYP, MP2, CCSD, and CCSD(T) levels were among the poorest performing methods based on accuracy. A wide range of Zn₂ equilibrium bond distances were predicted, indicating that many of the studied levels of theory may be unable to adequately describe this transition metal dimer. To further benchmark the accuracy of the density functional methods, high-level CASSCF and CASPT2 calculations were performed to estimate bond dissociation energies, equilibrium bond lengths, and heats of formation for the diatomic Zn complexes, and the latter two quantities were compared with the results of DFT, MP2, and coupled-cluster calculations as well as experimental values.



INTRODUCTION

Heat of formation is an experimentally determinable physical property of molecules used in the benchmarking of computational methodologies. Recently, we have assessed the abilities of various approaches in the prediction of heats of formation for transition metal complexes using the 6-31G** and TZVP basis sets on all atoms, as well as the LANL2DZ basis set/pseudopotential on zinc (with both 6-31G** and TZVP on the nonmetal atoms) using both density functional and coupled-cluster methods.^{1–3}

Considerable attention has been given recently to theoretical studies on the properties of transition metals and their systems. Given its rich chemistry, zinc has received more than its fair share of attention. For example, Balabanov and Peterson have used nonrelativistic and Douglas–Kroll–Hess relativistic cc-pVnZ basis sets that converge to the CBS limit to accurately obtain atomic excitation energies, ionization potentials, and electron affinities for third row metal atoms and several metal hydrides.⁴ Eger et al. used density functional to study the mechanism of the zinc carbenoid-mediated homologation of β -keto esters.⁵ In 2009, van Gastel et al. complemented their EPR/ENDOR study of bis(a-aminopyridinato)zinc with B3LYP/TZV calculations used to support experimental determination of the proton

hyperfine coupling constants.⁶ In yet another application, Govind and co-workers utilized TDDFT calculations in order to probe the excitation energies of zinc porphyrin in aqueous solution.⁷ Jenovine and Spezia used density functional theory, as well as MP2 and CCSD(T) calculations, to study binding in transition metal chalcogen–chalcogen bridges, noting in these instances the seemingly consistent failure of DFT in its overestimation of the binding energy.⁸ Schmidt et al. have used computations to aid in the characterization of new zinc amidinate complexes.⁹ Some validation work in the area has been recently published; Sorkin et al. benchmarked the performance of four density functionals and six semiempirical methods against experimental bond distances, angles, dipole moments, and dissociation energies.¹⁰

Despite the amount of attention given to calculations on zinc systems, comparably little attention has been given to benchmarking the performance of a wide range of levels, particularly with larger basis sets over a range of metal–ligand bond types. Jiang et al. used DFT methods in combination with correlation consistent basis sets to evaluate heats of formation for transition metal complexes, although the overlap in their selected

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functionals and those incorporated in the study herein is limited.¹¹ An earlier study by Tekarli et al. incorporated 44 density functionals and the cc-pVTZ and cc-pVQZ basis sets to compute heats of formation; however, this work investigated only four zinc-containing complexes.¹²

Heats of formation have been calculated using a variety of computational strategies over the past two decades, with the level of complexity in the methods employed increasing as new protocols are developed and computing power has increased. One of the more popular approaches is the geometry optimization/complete basis set (CBS) extrapolation method. Pollack et al. used this strategy to very accurately produce the enthalpies of formation for several alkanes using B3LYP/TZVP and MP2/aug-cc-pVTZ geometries.¹³ While it is generally accepted that B3LYP offers exceptional performance for organic compounds, this level of confidence cannot be carried over to transition metal complexes, hence the need for further validation in the arena of computational chemistry regarding the transition metal elements.

In furthering our studies on the calculation of heats of formation for ZnX complexes, we have conducted calculations using the correlation consistent, triple- ζ quality cc-pVTZ and aug-cc-pVTZ basis sets with density functional methods, as well as the MP2, CCSD, and CCSD(T) methods, and compared the results against experimentally determined values. The DFT methods utilized include functionals of the GGA (BLYP,^{14,15} MPWPW91,^{16–18} PBEPBE¹⁹), hybrid-GGA (B3LYP,^{14,15,20,21} PBE1PBE,^{19,22,23} B98²⁴), meta-GGA (TPSSPTSS,^{25,26} TPSSKCIS,^{25–29} BB95^{14,30}), and hybrid-meta-GGA (B1B95,^{14,30} TPSS1KCIS,^{25–29,31} BB1K^{14,30,32}) classes (occupying rungs two through four of Perdew's "Jacob's Ladder" of density functionals)^{33,34} as in our previous studies. Additionally, we have selected for comparison the M06-L³⁵ (meta-GGA) and M06-2X³⁶ (hybrid-meta-GGA) functionals of Truhlar et al., as these functionals have become available in the Gaussian suite since our previous work. Zinc complexes considered in this study are Zn₂, ZnH, ZnO, ZnF₂, ZnS, ZnCl, ZnCl₂, ZnCH₃, and Zn(CH₃)₂. The aims of this work are 2-fold: one, to evaluate the ability of different models to accurately and cost-effectively predict heats of formation and reproduce geometries and, two, to identify appropriate levels of theory for the determination of zinc force field parameters.³⁷ In the simplest of terms, we wish to explore the generality of various levels of theory applied to Zn systems with different ligating atoms using calculated bond lengths and predicted heats of formation as our evaluation criteria. Finally, for the dimeric species, we compare the results to CASPT2 derived bond lengths and heats of formation as a further benchmark.

■ COMPUTATIONAL METHODOLOGY

All DFT, MP2, and coupled-cluster calculations were carried out on a SUN cluster featuring dual 2.5 GHz Opteron nodes or a twin node cluster featuring 2.6 GHz CPUs using the Gaussian 09³⁸ suite of programs. Calculations utilized up to 12 processors for some of the larger calculations. 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, as SCF convergence was often problematic in the initial stages of geometry optimization. The CCSD and CCSD(T) methods were used as implemented in Gaussian 09.^{39–44} Frequency calculations were conducted on all optimized geometries (at the minimum energy multiplicity) to ensure all calculated lowest

energy structures resided at local minima on their respective potential energy surfaces. The correlation consistent cc-pVTZ and aug-cc-pVTZ basis sets were used as implemented in Gaussian 09 for Zn and all nonmetal atoms.^{4,45,46}

The lowest energy conformations for all complexes as determined in our previous work were submitted for geometry optimization. The singlet and triplet states for ZnO and ZnS were both optimized, as these states were found to possess close energies, and different theory levels were found to result in the prediction of either multiplicity as the ground state. CCSD(T) calculations on ZnMe₂ were cost prohibitive, and these optimizations were not conducted using either the cc-pVTZ or aug-cc-pVTZ basis sets.

Additionally, all dimers were optimized using both the CASSCF and CASPT2 methods. All CASSCF/PT2 calculations were performed using the MOLCAS-7.7 package.⁴⁷ Basis sets of the atomic natural orbitals (ANO-RCC)^{48,49} type from the MOLCAS library were employed for all elements. The basis set employed for the zinc atom is derived from 21s15p10d6f4g2h primitive basis sets. Atomic natural orbital (ANO) type contractions were performed with 10s9p8d6f4g2h. For the oxygen atom, the primitive set of 14s9p4d3f2g functions was contracted to 8s7p4d3f2g. The hydrogen atom has the primitive basis set of 8s4p3d1f with a contraction of 6s4p3d1f. For the chlorine and sulfur atoms, the primitive set of 17s12p5d4f2g was contracted to 8s7p5d4f2g.

The following active spaces were employed. For ZnH, an active space of three electrons in nine orbitals (3,9) was employed. These orbitals are linear combinations of Zn 4s4p and H 1s2s2p orbitals. For Zn₂, an active space of (4,10), which arises from Zn 4s4p5s orbitals, was selected. For ZnO an active space of (8,17), arising from linear combinations of Zn 4s4p and O 2s2p3s3p3d orbitals, was employed. For ZnS, an active space of (8,17), arising from Zn 4s4p and S 3s3p3d4s4p orbitals, was used, and for ZnCl, an active space of (7,12) was used, which are linear combinations of Zn 4s4p and Cl 3p3d orbitals. At the CASPT2 level, an imaginary level shift of 0.1 was used.⁵⁰

The default ionization potential electron affinity (IPEA)-corrected zeroth-order Hamiltonian⁵¹ was used in CASPT2, corresponding to a IPEA shift of 0.25, unless otherwise specified (see the section on Zn₂). The orbitals correlated in the CASPT2 calculations for each species are reported in the results section.

D_{2h} symmetry was imposed upon the metal dimer, whereas C_{2v} symmetry was applied to the other diatomic molecules. The spectroscopic constants for the ground states of the investigated complexes were obtained using the MOLCAS program VIBROT fitting the potentials to the vibrational Schrödinger equation numerically. In subsequent heat of formation determinations, the CASPT2 energies were augmented by adding the thermal enthalpy correction from the corresponding CCSD(T)/cc-pVTZ calculation.

As in our previous studies, heats of formation (ΔH_f) for all complexes were computed with the method outlined in the Gaussian white paper on thermochemistry available in the Gaussian 09 online manual.⁵² For convenience, we show eq 1, which is the more general form, and eq 2, which expresses quantities in terms of the Gaussian output. The M and x designations in eq 1 correspond to the molecule and individual atoms, respectively.

$$\begin{aligned} \Delta H_f(M, 298 \text{ K}) &= \Delta H_f(M, 0 \text{ K}) \\ &+ ((H_M(298 \text{ K}) - H_M(0 \text{ K})) \\ &- \sum x(H_x(298 \text{ K}) - H_x(0 \text{ K}))) \quad (1) \end{aligned}$$

Table 1. Experimental,⁵⁴ DFT, MP2, CCSD, and CCSD(T) Heats of Formation for Zn Complexes^a

method	ΔH_f								
	Zn ₂	ZnH	ZnO	ZnF ₂	ZnS	ZnCl	ZnCl ₂	ZnCH ₃	Zn(CH ₃) ₂
expt.	57.7	62.9	52.8	−118.9	48.7	6.5	−63.5	26	12.9
expt. error	1.5	0.5	0.9	1.1	3.0	1.0	0.4	2.5	2.0
BLYP	65.0	64.2	51.5	−116.2	67.1	16.7	−48.9	55.9	26.1
MPWPW91	63.5	62.7	48.2	−122.9	61.0	9.3	−61.2	48.7	12.5
PBEPBE	62.9	62.9	46.4	−125.1	59.5	8.5	−63.7	46.2	7.0
B3LYP	64.9	62.6	61.3	−111.2	69.4	14.2	−53.0	52.9	19.9
PBE1PBE	63.6	61.4	58.7	−114.1	64.4	6.8	−64.7	49.0	13.8
B98	64.0	64.3	61.5	−114.7	64.5	11.6	−61.3	53.8	19.5
TPSSTPSS	63.1	56.8	51.9	−122.2	59.8	6.6	−64.7	43.4	4.0
TPSSKCIS	63.6	60.3	50.3	−121.6	60.3	8.1	−62.1	47.2	11.2
BB95	64.5	64.2	45.3	−125.5	59.0	11.0	−61.1	51.2	14.9
B1B95	64.7	62.8	61.4	−114.7	63.8	8.7	−63.6	52.9	19.2
TPSS1KCIS	64.0	59.9	57.7	−116.0	62.9	7.6	−62.3	48.0	13.1
BB1K	64.8	61.8	72.8	−110.6	65.7	7.1	−65.4	53.2	20.5
M06-L	62.8	62.3	49.6	−133.5	55.7	5.3	−76.0	42.6	−6.5
M06-2X	64.3	62.4	68.5	−117.3	66.0	6.3	−65.5	50.8	18.8
MP2	64.4	63.7	45.1	−129.1	62.2	5.3	−69.0	55.3	23.2
CCSD	64.9	62.4	71.8	−107.6	74.9	13.2	−54.0	61.9	37.2
CCSD(T)	64.8	62.9	61.4	−111.7	69.2	12.3	−57.1	58.4	

^aAll calculations use the cc-pVTZ basis set. All values are in kcal mol^{−1}.

$$\begin{aligned} \Delta H_f(298 \text{ K}) &= 627.5095(E_{\text{CORR}}) + 31.17 \\ &- 627.5095(E_{\text{Zn}}) + \Delta H_f(\text{atom}, 298 \text{ K}) \\ &- 627.5095(E_{\text{atom}}) \end{aligned} \quad (2)$$

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,⁵³ and the respective ΔH_f (atom, 298 K) values for the nonmetals are contained there as well. Finally, eq 3 was implemented in the calculation of root mean squared deviations (RMSD). RMSD values calculated for the ΔH_f error at each level of theory are available in the Supporting Information.

$$\sqrt{\frac{1}{n} \sum_i^n (x_i - \bar{x})^2} \quad (3)$$

RESULTS AND DISCUSSION

Heats of Formation. Calculated heats of formation for all methods with the cc-pVTZ basis set are shown in Table 1, with the average error associated with each method displayed in Figure 1. The CCSD(T) entry for Zn(CH₃)₂ is blank, as these calculations became cost-prohibitive. All other ΔH_f values were successfully calculated at each level of theory for each ZnX complex. The TPSSKCIS and TPSSTPSS density functionals were the two best overall methods for predicting heats of formation based on the average unsigned error. Of the DFT methods, BLYP and B3LYP functionals were the two poorest overall choices, with average unsigned errors over 10 kcal/mol. The MP2, CCSD, and CCSD(T) methods produced some of the poorer overall results, with the CCSD/cc-pVTZ level of theory providing the worst overall results.

ZnH was the most consistently well-calculated species, with most methods producing results within 2 kcal/mol of the

experimental value. Two of the greatest deviations from the experimental heat of formation for the hydride were observed with the TPSSTPSS and TPSSKCIS density functionals, the two methods producing the best overall results based on average unsigned error. For all other nonmethyl species, the TPSSTPSS and TPSSKCIS functionals were among the best performing methods.

The heat of formation for ZnCH₃ was consistently very poorly calculated by all methods using the cc-pVTZ basis set. The TPSSTPSS/cc-pVTZ level of theory came the closest to the experimental value but still deviated by 17.4 kcal/mol, a 67% error. Zn(CH₃)₂ fared slightly better, with the PBEPBE, PBE1PBE, and TPSS1KCIS density functionals all producing results within 1 kcal/mol of the experimental value. However, most deviations were significantly large, and the CCSD(T) calculations could not be performed, as the computational cost was prohibitive.

Table 2 and Figure 2 contain results for all methods using the aug-cc-pVTZ basis set. These calculations were naturally more costly than those using the cc-pVTZ basis set, and calculations utilizing both coupled cluster methods proved to be cost prohibitive for Zn(CH₃)₂. With this basis set, the CCSD level of theory was the poorest overall for predicting ΔH_f values, and the MP2 level outperformed only BLYP and CCSD. The CCSD(T)/aug-cc-pVTZ level of theory yielded a low average unsigned error and outperformed all but four of the density functional methods; however the fact that the calculations on Zn(CH₃)₂ were not completed needs to be taken into consideration when evaluating the overall efficacy of this level.

Bond Lengths. Tables 3 and 4 contain the calculated Zn–X bond lengths for the studied ZnX systems using the cc-pVTZ and aug-cc-pVTZ basis sets, respectively. The Zn–F bond length for ¹ZnF₂ was very accurately calculated by all methods, with the largest deviation from the experimental observed at the BB1K/cc-pVTZ and MP2/cc-pVTZ levels of theory (0.020 and 0.022 Å underestimations, respectively). The largest overestimation was observed at the BLYP/aug-cc-pVTZ level of theory, at 0.012 Å. The deviations from the experimental Zn–F length spanned a

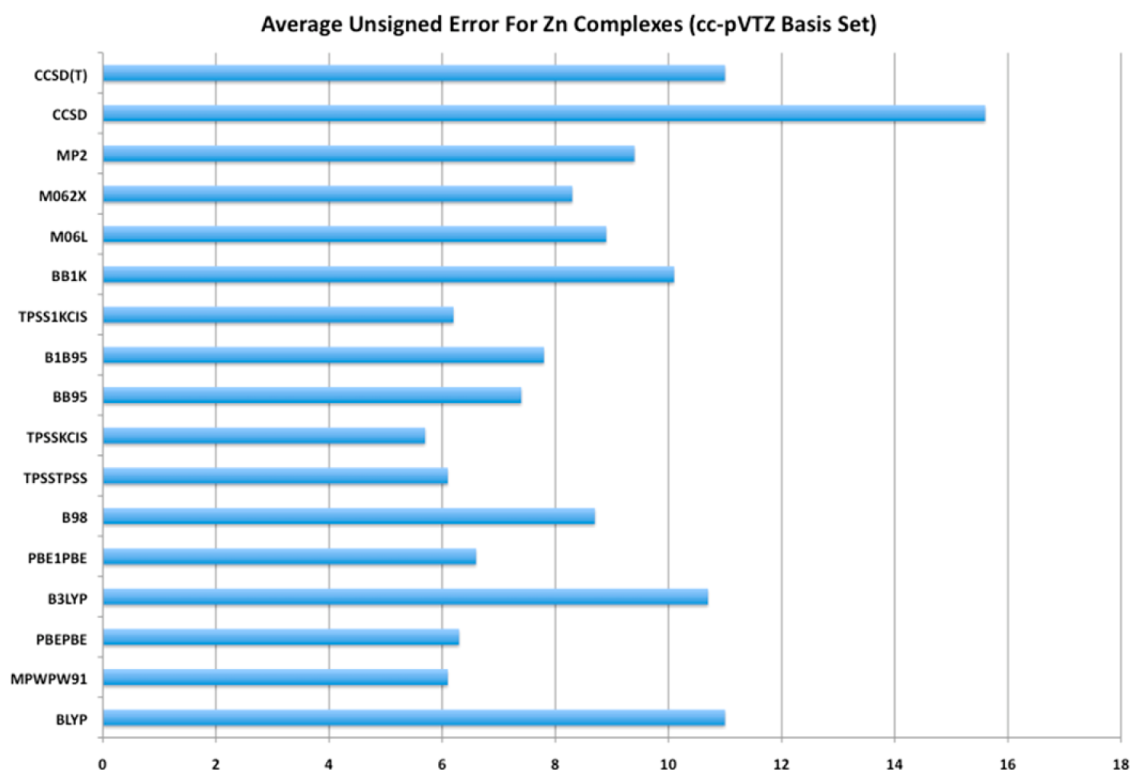


Figure 1. Average unsigned error (kcal/mol) for all methods using the cc-pVTZ basis set. The CCSD(T) errors are an average of the eight calculable complexes.

Table 2. Experimental,⁵⁴ DFT, MP2, CCSD, and CCSD(T) Heats of Formation for Zn Complexes^a

method	ΔH_f								
	Zn ₂	ZnH	ZnO	ZnF ₂	ZnS	ZnCl	ZnCl ₂	ZnCH ₃	Zn(CH ₃) ₂
expt.	57.7	62.9	52.8	−118.9	48.7	6.5	−63.5	26	12.9
expt. error	1.5	0.5	0.9	1.1	3.0	1.0	0.4	2.5	2.0
BLYP	65.2	64.4	50.6	−118.4	67.1	16.6	−49.0	56.4	26.8
MPWPW91	63.7	62.8	47.2	−125.3	61.0	9.2	−61.5	49.1	13.2
PBEPBE	63.2	63.0	45.4	−127.6	59.5	8.3	−64.0	46.7	7.8
B3LYP	65.0	62.7	60.4	−114.4	30.7	13.9	−53.5	53.1	20.2
PBE1PBE	63.7	61.5	62.2	−117.7	64.1	6.3	−65.5	49.1	14.1
B98	64.1	64.4	60.4	−118.2	64.2	11.1	−62.1	54.0	19.9
TPSSTPSS	63.4	56.9	50.8	−125.1	59.7	6.4	−65.2	43.8	4.7
TPSSKCIS	63.9	60.4	49.2	−124.4	60.2	7.9	−62.4	47.6	12.0
BB95	64.7	64.4	44.4	−127.9	58.9	10.8	−61.4	51.7	15.7
B1B95	64.8	62.8	62.4	−118.3	63.4	8.2	−64.4	53.0	19.4
TPSS1KCIS	64.1	60.0	56.7	−119.3	62.6	7.2	−62.9	48.2	13.6
BB1K	64.8	61.8	70.6	−114.7	65.2	6.6	−66.4	53.2	20.5
M06-L	63.2	65.8	58.4	−118.5	61.7	8.9	−69.4	54.4	17.0
M06-2X	64.3	62.2	65.7	−121.6	65.2	5.5	−66.7	50.6	18.1
MP2	64.0	64.8	40.2	−137.4	60.6	4.8	−71.6	54.8	20.4
CCSD	64.7	62.6	67.8	−115.8	73.2	11.9	−57.0	60.5	
CCSD(T)	64.6	63.2	57.3	−120.4	67.4	11.0	−60.3	38.9	

^aAll calculations use the aug-cc-pVTZ basis set. All values are in kcal mol^{−1}.

0.034 Å range, the lowest span of the four entries for which experimental bond distances were available.

Greater discrepancies were observed in the predicted bond lengths for ²ZnH. The variation for ²ZnH ranged from an underestimation of 0.028 Å at the MP2/cc-pVTZ level of theory to a 0.051 Å overestimation at the M062X/cc-pVTZ level. The addition of diffuse functions did not significantly reduce the latter overestimation, as M06-2X/aug-cc-pVTZ calculations predicted a

0.050 Å overestimation of the Zn–H bond length. Hence, predicted values for the Zn–H bond length cover a 0.079 Å range, supporting the argument that improper consideration of the employed level of theory can have significant geometric consequences.

Only the MP2 method underestimated the Zn–Cl distance for ¹ZnCl₂, by 0.002 Å with the cc-pVTZ basis set and 0.004 Å with the inclusion of diffuse functions. The M06-2X functional overestimated the Zn–Cl distance by the greatest amount, 0.038 Å

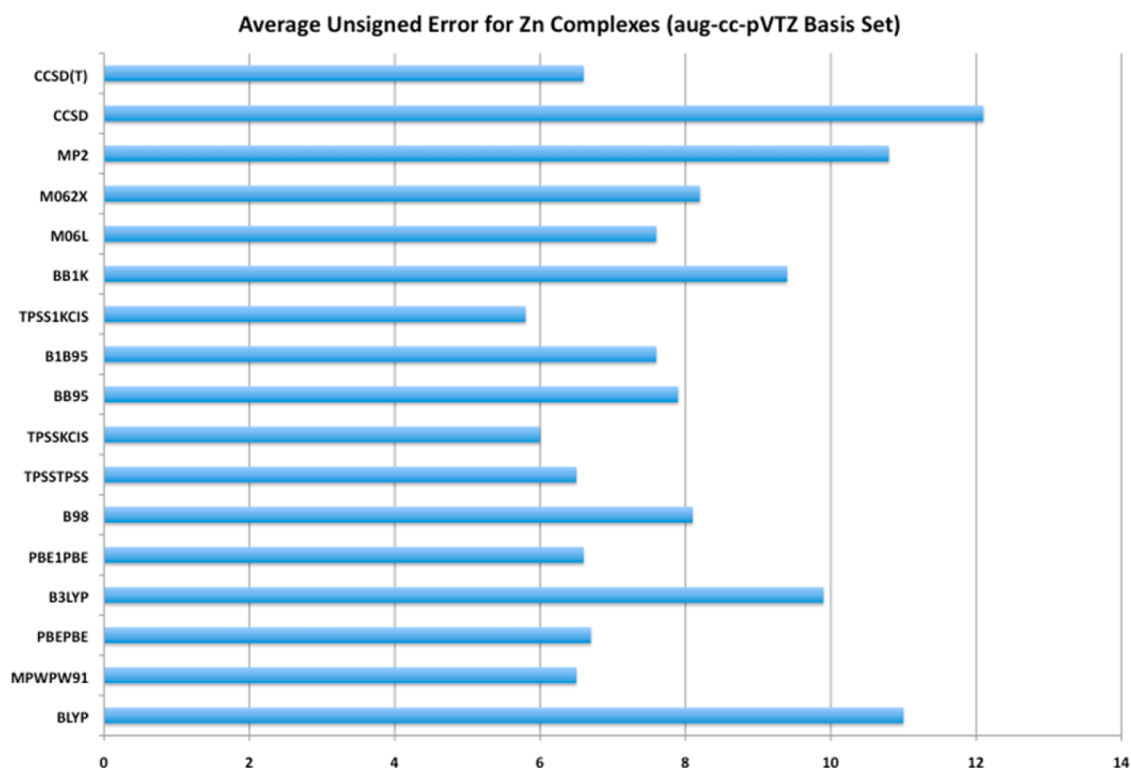


Figure 2. Average unsigned error (kcal/mol) for all methods using the aug-cc-pVTZ basis set. The CCSD and CCSD(T) errors are an average of the eight calculable complexes.

Table 3. Experimental,⁵⁵ DFT, MP2, CCSD, and CCSD(T) Zn–X Bond Lengths (Ångstroms) for Zn Complexes, cc-pVTZ Basis Set^a

method	Zn ₂	ZnH	ZnO	ZnF ₂	ZnS	ZnCl	ZnCl ₂	ZnCH ₃	Zn(CH ₃) ₂
expt.	4.19 ⁵⁶	1.594		1.742	2.046	2.130	2.072		1.930
BLYP	3.628	1.635	1.713	1.749	2.084	2.202	2.108	2.079	1.968 ^d
MPWPW91	3.161	1.615	1.699	1.739	2.060	2.168	2.088	2.033	1.948 ^b
PBEPBE	3.148	1.618	1.698	1.739	2.059	2.167	2.087	2.031	1.947 ^b
B3LYP	3.740	1.621	1.880 ^e	1.736	2.073	2.179	2.096	2.054	1.958 ^b
PBE1PBE	3.290	1.609	1.857 ^e	1.727	2.052	2.152	2.081	2.015	1.942 ^c
B98	3.544	1.622	1.881 ^e	1.735	2.071	2.176	2.095	2.051	1.958 ^b
TPSSTPSS	3.080	1.609	1.696	1.736	2.053	2.164	2.086	2.032	1.950 ^b
TPSSKCIS	3.200	1.609	1.701	1.740	2.059	2.172	2.091	2.040	1.954 ^c
BB95	3.267	1.623	1.701	1.741	2.059	2.173	2.088	2.040	1.948 ^b
B1B95	3.529	1.611	1.863 ^e	1.727	2.050	2.153	2.079	2.020	1.942 ^c
TPSS1KCIS	3.303	1.606	1.867 ^e	1.734	2.056	2.164	2.088	2.032	1.951 ^c
BB1K	3.632	1.607	1.692	1.722	2.045	2.146	2.076	2.010	1.940 ^c
M06-L	3.202	1.618	1.699	1.730	2.045	2.157	2.075	2.036	1.945 ^b
M06-2X	3.967	1.645	1.723	1.741	2.099	2.184	2.110	2.057	1.978 ^b
MP2	3.904	1.566	1.665	1.720	2.043	2.129	2.070	1.975	1.924 ^c
CCSD	4.856	1.597	1.718	1.726	2.071	2.150	2.090	2.013	1.949 ^c
CCSD(T)	4.488	1.594	1.711	1.727	2.070	2.148	2.088	2.010	

^aCalculation required OPT=CalcAll. ^bEclipsed. ^cGauche. ^dOffset. ^eIndicates those methods predicting a ground state triplet for ZnO, as opposed to the singlet state.

with both basis sets. Overall, the deviations from the experimental distance spanned a 0.042 Å range; however the majority of the methods employed adequately predict the observed bond length for ¹ZnCl₂.

Finally, we consider ¹Zn(CH₃)₂, which was impractical for CCSD(T) using both basis sets and at the CCSD/aug-cc-pVTZ level of theory. For the remaining methods, MP2 calculations using both basis sets underestimated the Zn–C bond length, and the DFT methods overestimated this value. Additionally, there is

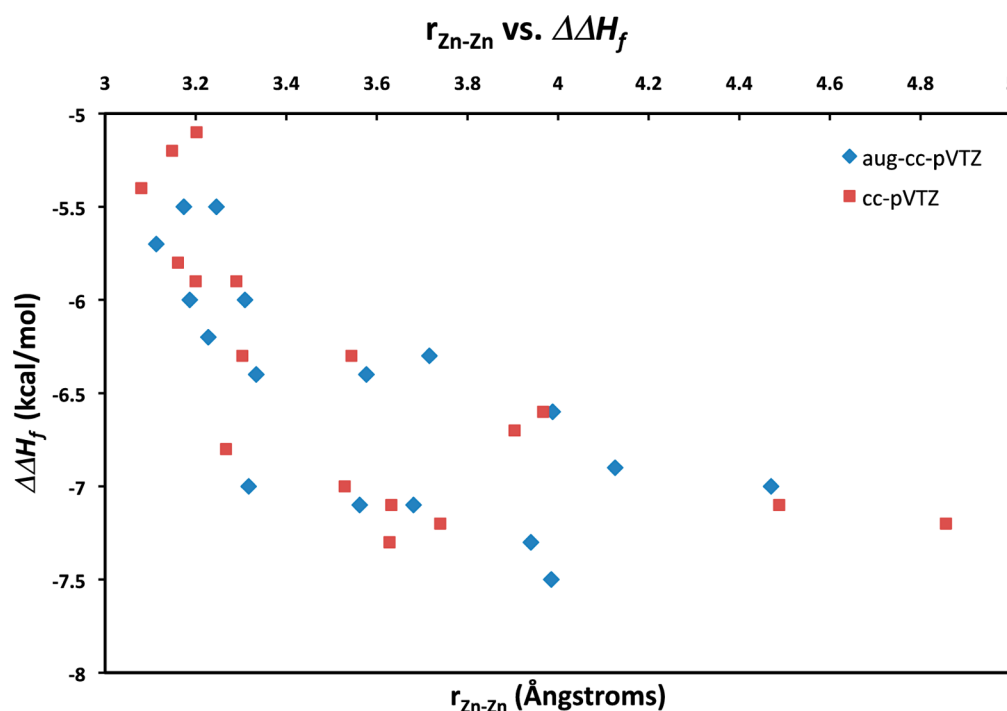
the issue of conformation. We previously addressed conformations in Zn(CH₃)₂ using smaller basis sets and found that typically at those levels this species adopts a “pseudo-eclipsed” conformation.² In this study, the minimum energy conformations varied among the employed methods, with “pseudo-eclipsed,” “pseudo-gauche,” and offset minima predicted.

For Zn₂, the calculated bond lengths using the cc-pVTZ basis set spanned a 1.776 Å range, an incredibly large value and reflective of the broad, flat nature of the potential energy surface.

Table 4. Experimental,⁵⁵ DFT, MP2, CCSD, and CCSD(T) Zn–X Bond Lengths (Ångstroms) for Zn Complexes, aug-cc-pVTZ Basis Set

method	Zn ₂	ZnH	ZnO	ZnF ₂	ZnS	ZnCl	ZnCl ₂	ZnCH ₃	Zn(CH ₃) ₂
expt.	4.19 ⁵⁶	1.594		1.742	2.046	2.130	2.072		1.930
BLYP	3.985	1.635	1.719	1.754	2.086	2.204	2.109	2.079	1.930
MPWPW91	3.187	1.615	1.703	1.743	2.061	2.089	2.089	2.032	1.967 ^c
PBEPBE	3.174	1.619	1.703	1.743	2.061	2.169	2.088	2.030	1.946 ^b
B3LYP	3.940	1.621	1.884 ^d	1.740	2.074	2.181	2.097	2.054	1.946 ^c
PBE1PBE	3.309	1.609	1.697	1.731	2.053	2.153	2.082	2.014	1.957 ^b
B98	3.577	1.622	1.706	1.739	2.072	2.178	2.096	2.050	1.942 ^b
TPSSTPSS	3.113	1.610	1.700	1.739	2.054	2.165	2.087	2.032	1.957 ^b
TPSSKCIS	3.228	1.609	1.706	1.743	2.060	2.173	2.092	2.040	1.950 ^b
BB95	3.317	1.623	1.706	1.745 ^a	2.061	2.174	2.089	2.039	1.954 ^b
B1B95	3.562	1.612	1.699	1.730	2.052	2.154	2.080	2.019	1.948 ^a
TPSS1KCIS	3.334	1.607	1.871 ^d	1.738	2.057	2.165	2.089	2.031	1.942 ^b
BB1K	3.681	1.607	1.696	1.725	2.047	2.147	2.077	2.010	1.951 ^b
M06-L	3.246	1.618	1.701	1.733	2.045	2.157	2.075	2.035	1.940 ^b
M06-2X	3.988	1.644	1.730	1.744	2.101	2.185	2.110	2.055	1.944 ^a
MP2	3.716	1.572	1.678	1.725	2.046	2.131	2.068	1.982	1.977 ^b
CCSD	4.470	1.604	1.723	1.730	2.072	1.152	2.088	2.018	1.925 ^b
CCSD(T)	4.126	1.603	1.719	1.732	2.072	2.151	2.086	2.018	

^aEclipsed. ^bGauche. ^cOffset. ^dIndicates those methods predicting a ground state triplet for ZnO, as opposed to the singlet state.

Figure 3. Zn–Zn bond length versus $\Delta\Delta H_f$ for all levels of theory investigated.

The shortest predicted bond length was 3.080 Å at the TPSSTPSS/cc-pVTZ level of theory, and the largest distance calculated was 4.856 Å at the CCSD/cc-pVTZ level. The addition of diffuse functions caused a contraction in the span between the minimum and maximum predicted Zn–Zn distance to 1.357 Å, which is still significantly large. As with the cc-pVTZ calculations, the shortest calculated bond length with the aug-cc-pVTZ basis set was predicted with the TPSSTPSS density functional (3.113 Å) and the largest with the CCSD method (4.470 Å). There is no strong correlation observed between the calculated bond length and the deviation from the experimental heat of formation; however the most general of trends is that shorter

bond lengths give decreased errors. These data are plotted in Figure 3 and separated by basis set. Given the wide range of calculated Zn–Zn bond lengths and the lack of available experimental data for this parameter, it is difficult to assess which methods are more appropriate for this transition metal dimer. It should be noted that an experimental value obtained for this distance using spectroscopic methods yields an equilibrium separation of 4.19 Å.⁵⁶ Earlier efforts at estimating this bond length yielded 4.8 and 4.67 Å using the Morse approximation and London dispersion relation, respectively.⁵⁷ Ellingsen et al. point out that all of these experimentally derived values are likely to be overestimates, as each method fails to account for the covalent character of the bond, instead assuming a purely

van der Waals interaction.⁵⁸ Furthermore, there is little direct correlation observed between calculated bond length and heat of formation error for either basis set, as evidenced by R^2 values of 0.472 and 0.508 for the cc-pVTZ and aug-cc-pVTZ basis sets, respectively. Despite the lack of a strong correlation it is, however, observed that theory levels yielding shorter Zn–Zn distances predict heats of formation closer to the experimental value.

The calculated bond distances for the remaining four entries (ZnO, ZnS, ZnCl, and ZnCH₃) spanned a much more reasonable range of values. For zinc oxide, different levels of theory predicted ¹ZnO and ³ZnO ground states; the singlet ground state was predicted the majority of the time for the 34 investigated theory levels. For methods where the triplet ground state was predicted, the optimized Zn–O bond length was noticeably longer than for those methods that predicted the singlet ground state. The addition of diffuse functions aided in predicting the singlet ground state. The B3LYP density functional incorrectly predicted the triplet ground state with both basis sets.

Multireference Character and Comparison with CASPT2 Calculations. Although CCSD(T) is considered a gold standard for single-reference methods, it is important to check how it behaves in the presence of multireference systems. For this reason, we report T_1 diagnostic values (Table 5) using

Table 5. CCSD/cc-pVTZ Computed T_1 Diagnostics for the Nine Zn Complexes

entry	CCSD/cc-pVTZ
¹ Zn ₂	0.0184
² ZnH	0.0211
¹ ZnO	0.0333
¹ ZnF ₂	0.0180
¹ ZnS	0.0241
² ZnCl	0.0167
¹ ZnCl ₂	0.0132
² ZnCH ₃	0.0174
¹ Zn(CH ₃) ₂	0.0128

the cc-pVTZ basis sets. The standard at which multireference effects are considered negligible is a T_1 value of 0.02 or less.^{59,60} As these values are dependent only upon the single excitations, the computed values will be the same regardless of whether the CCSD or CCSD(T) methods is implemented.⁵⁹ Jiang et al. computed the T_1 diagnostic of the Zn dimer using coupled cluster methods (cc-pVTZ-DK basis set), and our results with the nonrelativistic cc-pVTZ basis set are consistent.^{61,62} The computed T_1 diagnostics using the cc-pVTZ basis set indicate that multireference functions are necessary for ZnH, ZnO, and ZnS. Furthermore, these values for Zn₂ and ZnF₂ are near the 0.02 threshold as well.

In order to check the degree of multireference character in these species, we report the following results obtained at the CASPT2 level of theory. Table 6 contains CASPT2 calculated equilibrium bond lengths, bond dissociation energies (D_e), harmonic vibrational frequencies (ω_e), and heats of formation for the zinc-containing dimers, together with the corresponding CCSD(T) values. The bond length predicted for the Zn dimer using 4s3d correlated electrons was lower than the experimental value listed and higher with only 4s correlated electrons. Since the reported experimental value is most likely an overestimation, the former calculated distance is likely more representative of the true value, and this length falls in line with the DFT methods

Table 6. Bond Lengths, Spectroscopic Constants, and Heats of Formation from CASPT2 Calculations on Zn Containing Dimers^a

entry	state	r_e (Å)	D_e (eV)	D_0 (eV)	ω_e (cm ⁻¹)	ΔH_f
Zn ₂ (3s3p3d4s)	¹ Σ_g^+	3.695	0.034	0.033	22.9	63.1
Zn ₂ (3p3d4s)	¹ Σ_g^+	4.704	0.034	0.032	23.6	63.1
Zn ₂ expt. ⁵⁸		4.19	0.035		25.9	57.7
CCSD(T) cc-pVTZ		4.488	0.010	0.009		64.8
CCSD(T) aug-cc-pVTZ		4.126	0.020	0.019		64.6
ZnO (Zn 3s3p3d4s) (O 2s2p)	¹ Σ^+	1.700	1.54	1.45	742	56.6
ZnO expt. ⁶³			1.61		805	52.8
CCSD(T) cc-pVTZ		1.711	1.34	1.29		61.4
CCSD(T) aug-cc-pVTZ		1.719	1.52	1.47		57.3
ZnH (Zn 3s3p3d4s)	² Σ^+	1.576	0.97	0.87	1644	63.8
ZnH expt. ⁶⁴		1.594	1.01		1603	62.9
CCSD(T) cc-pVTZ		1.594	1.01	0.91		62.9
CCSD(T) aug-cc-pVTZ		1.603	0.99	0.90		63.2
ZnS (Zn 3s3p3d4s) (S 2s2p3s3p)	¹ Σ^+	2.047	2.59	2.54	488	65.0
ZnS expt. ⁶⁵		2.046	3.12		457	48.7
CCSD(T) cc-pVTZ		2.070	1.28	1.25		69.2
CCSD(T) aug-cc-pVTZ		2.072	1.36	1.33		67.4
ZnCl (Zn 3s3p3d4s) (S 2s2p3s3p)	² Σ^+	2.113	2.17	2.32	404	11.5
ZnCl expt. ⁶⁶		2.130	2.73		385.2	6.5
CCSD(T) cc-pVTZ		2.148	2.13	2.11		12.3
CCSD(T) aug-cc-pVTZ		2.151	2.19	2.17		11.0

^aCorrelated electrons in the CASPT2 calculations are indicated in parentheses. The corresponding CCSD(T) values are also included for comparison.

employed. The calculated ZnH, ZnCl, and ZnS bond lengths show excellent agreement with experimental data. The D_e values predicted by both Zn₂ calculations were in excellent agreement with the experimental value. Similar agreement was observed between calculated and experimental bond dissociation energy for ZnO and ZnH, whereas the calculated ZnCl and ZnS D_e values were significant underestimations. The ω_e value calculated for ZnH showed excellent agreement with the experimental frequency, with a 2.6% deviation. The ZnCl and ZnS calculated ω_e values showed moderate agreement with experimental results, with respective 4.9 and 6.8% errors. The 63 wavenumber error between computed and observed ω_e for ZnO represents a –7.8% deviation. Finally, while the absolute error in the Zn₂ calculated values was small, the percentage errors were significant, regardless of the selected correlated electrons (–11.6% with 3s3p3d4s and –8.9% with 3p3d4s). In Table 6, we have also reported the CCSD(T) values for r_e and ΔH_f for comparison. As far as ΔH_f is concerned, CASPT2 and CCSD(T) yield similar results for the Zn complexes investigated, with the CASPT2 values offering slight improvements over the CCSD(T) values for Zn₂, ZnO, and ZnS. The predicted value for ZnH is outside the experimental error range and poorer than the values predicted with both basis sets using the CCSD(T) method. Finally, in the case of ZnCl, the CASPT2 predicted heat of formation lies between the values predicted at the CCSD(T)/cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels of theory.

CONCLUSIONS

Heats of formation were calculated for nine ZnX complexes using 14 density functionals, and the MP2, CCSD, and CCSD(T) methods with both the cc-pVTZ and aug-cc-pVTZ

basis sets. CASPT2 energies were used to predict heats of formation for all dimeric Zn complexes. Among the poorest performing levels of theory were BLYP, B3LYP, MP2, and CCSD. CCSD(T) proved acceptable in conjunction with the aug-cc-pVTZ basis set, besting all but four of the density functional methods employed; however, the calculations on $\text{Zn}(\text{CH}_3)_2$ proved to be cost prohibitive (for both basis sets), which limits the overall efficacy of the method. The TPSSKCIS/cc-pVTZ level of theory produced the lowest unsigned average error for predicted heats of formation. Other low error theory levels include TPSS1KCIS/aug-cc-pVTZ and TPSSSTPSS, MPWPW91, PBEPBE, and PBE1PBE with the cc-pVTZ basis set (identical or slightly larger average unsigned errors were observed with the inclusion of diffuse functions).

Additionally, the calculated distances at the various levels of theory employed were compared to experimental values. An exceptionally large range of Zn–Zn bond lengths was calculated for Zn_2 , with the coupled cluster values by far the largest. The bond lengths calculated using the TPSSSTPSS density functional with both basis sets were the smallest values and the CCSD/cc-pVTZ distance the largest. In general, some of the largest deviations from experimental bond lengths were observed with the B3LYP functional.

These results support our previous conclusions^{2,3} that for studying systems employing zinc centers, careful consideration should be paid to the chosen density functional method even with these larger basis sets and that properly selected density functionals clearly outperform MP2 and coupled-cluster calculations. CASPT2 energies with CCSD/cc-pVTZ thermal corrections produced experimentally accurate heats of formation for ZnH , ZnO , and ZnCl , although clearly this theory level is not plausible for biologically relevant systems.

■ ASSOCIATED CONTENT

■ Supporting Information

Spreadsheets detailing atom energies, complex energies, ground state multiplicities, and heat of formation calculations for all Zn complexes at each investigated level of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: kmerz1@gmail.com.

*E-mail: gagliard@umn.edu.

Notes

The authors declare no competing financial interest.

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