Computational *s*-Block Thermochemistry with the Correlation Consistent Composite Approach

Nathan J. DeYonker, Dustin S. Ho, Angela K. Wilson,* and Thomas R. Cundari*

Center for Advanced Scientific Computing and Modeling, Department of Chemistry, University of North Texas, Denton, Texas 76203-5070

Received: May 11, 2007; In Final Form: July 2, 2007

The correlation consistent composite approach (ccCA) is a model chemistry that has been shown to accurately compute gas-phase enthalpies of formation for alkali and alkaline earth metal oxides and hydroxides (Ho, D. S.; DeYonker, N. J.; Wilson, A. K.; Cundari, T. R. *J. Phys. Chem. A* **2006**, *110*, 9767).The ccCA results contrast to more widely used model chemistries where calculated enthalpies of formation for such species can be in error by up to 90 kcal mol^{-1}. In this study, we have applied ccCA to a more general set of 42 *s*-block molecules and compared the ccCA ΔH_f values to values obtained using the G3 and G3B model chemistries. Included in this training set are water complexes such as $Na(H_2O)_n^+$ where $n = 1 - 4$, dimers and trimers of ionic compounds such as $(LiCl)_2$ and $(LiCl)_3$, and the largest ccCA computation to date: Be(acac)$_2$, $BeC_{10}H_{14}O_4$. Problems with the G3 model chemistries seem to be isolated to metal−oxygen bonded systems and Be-containing systems, as G3 and G3B still perform quite well with a 2.7 and 2.6 kcal mol^{-1} mean absolute deviation (MAD), respectively, for gas-phase enthalpies of formation. The MAD of the ccCA is only 2.2 kcal mol^{-1} for enthalpies of formation (ΔH_f) for all compounds studied herein. While this MAD is roughly double that found for a ccCA study of >350 main group (i.e., *p*-block) compounds, it is commensurate with typical experimental uncertainties for *s*-block complexes. Some molecules where G3/G3B and ccCA computed ΔH_f values deviate significantly from experiment, such as $(LiCl)_3$, NaCN, and MgF, are inviting candidates for new experimental and high-level theoretical studies.

Introduction

Compounds containing alkali and alkaline earth metals are commonplace within the body, nature, chemistry laboratory, and chemical industry. The electronic structure and thermochemistry of gas-phase *s*-block materials has been recently investigated for a variety of applications, for example, theoretical comparison to Li^+-attachment mass spectrometry experiments,[1−4] formation of sodium and magnesium bicarbonate in cloud nucleation,[5,6] binding studies of amino acids[7] or π-complexes with metal cations,[3,8] and discerning trends in the bonding and reactivity of organometallic reagents.[9] These studies have proven to be generally successful and employ a variety of density functional theory (DFT) and molecular orbital (MO) based methods.

Among the most popular ab initio methods are the Gaussian-*n*, or G*n*, methods of Pople, Curtiss, Redfern, Raghavachari, and co-workers[10−21] as well as the W*n* methods of Martin and co-workers.[22−26] These two families of methods are called composite methods, in that the total energy of a system is obtained using additive approximations of basis set and electron correlation effects obtained from multiple computations of greater efficiency. The additive corrections in G*n* methods are based upon small basis set fourth-order Møller−Plesset perturbation energy single-point calculations, while W*n* is based upon coupled cluster additive corrections. The G3 method, which is the standard implementation of G*n* methods, predicts energetic quantities (enthalpies of formation, ionization potentials, electron affinities, proton affinities, isomerization energies, etc.) within 1−2 kcal mol^{-1} of the experimental value.[27−29] The W*n* methods are more sophisticated and computationally expensive, with a typical accuracy of 0.5−1.0 kcal mol^{-1}.[23,25,26]

Well-documented examples where the G*n* and W*n* families of model chemistries perform unreliably are for systems containing alkali and alkaline earth metal elements. A number of investigations of enthalpies of formation and cation affinities of *s*-block compounds provides the most egregious deviations for these otherwise successful composite methods.[30−34] The magnitude of the deviations, up to 90 kcal mol^{-1} as compared to experiment for these model chemistries, is quite disturbing. Deficiencies that these composite methods have in computing *s*-block enthalpies of formation are proposed to be due largely to the treatment of the core−valence electron correlation and geometry-dependent valence correlation effects. The computed G3 and W2 enthalpies of formation are sufficiently accurate when the core−valence correlation (or all-electron correlation) is included in all single-point energy computations and a rather expensive level of theory [CCSD(T) with core electrons correlated and a quadruple-ζ-sized basis set] is used for optimization of the geometry.[24] Also, for the G3 methods, the semiempirical high-level correction (HLC) needed reparametrization to achieve chemical accuracy (viz. 1−2 kcal mol^{-1}). These modifications go against the fundamental reasons as to why composite methods are inherently useful; the modifications require in-depth knowledge of the software package, and these modifications can render the composite method as expensive as large basis set coupled cluster model chemistries. Since a study carried out by Petrie warned of potential shortcomings when applying the G*n* methods to *s*-block molecules,[31] a number of modified G*n* methods have been created specifically for such

* Corresponding authors. E-mail: (A.K.W.) akwilson@unt.edu and (T.R.C.) tomc@unt.edu.

10.1021/jp0736241 CCC: $37.00 © 2007 American Chemical Society
Published on Web 10/03/2007

species. The most notable of these, CP-dG2(thaw) and G3-GCP, use geometry corrected counterpoise corrected energies.[30,31,34−36] Also, for molecules containing Na or Mg, a thawed correlation space where the 2s and 2p outermost core orbitals are correlated is used in all of the energy computations. However, it has been shown recently that G*n* HLC primarily accounts for basis set incompleteness effects.[37] Therefore, it seems unusual that the basis set superposition error (BSSE) is problematic for these *s*-block systems.

Our new model chemistry, called the correlation consistent composite approach (ccCA),[37−39] uses DFT equilibrium geometries and scaled harmonic vibrational frequencies. Upon these stationary points, standard correlation consistent basis sets are used to extrapolate MP2 energies to the complete basis set (CBS) limit, and additive corrections are computed. The current implementation of ccCA has been found to be as accurate as the G3X composite method for the G3/99 training set despite the lack of a HLC for the former.[39]

The application of ccCA toward the *s*-block oxides and hydroxides proved to be successful in a preliminary study.[40] For the eight molecules investigated, the standard implementations of the ccCA model chemistry mostly predicted ΔH_f values within the error bars of recommended enthalpies of formation derived from computationally expensive large basis set coupled cluster computations. The ccCA model chemistry was shown to be as accurate as the modified G*n* and W*n* methods in ref 24, as well as much more computationally efficient than the large basis set coupled cluster energies required by such modifications.

In this study, we show ccCA to be a robust and reliable method for computing *s*-block energetic properties by computing the enthalpies of formation for all *s*-block-containing molecules that are found in the comprehensive training set of 600 molecules devised by Cioslowski and co-workers.[41] Within this test set, there are 39 molecules containing Li, Be, Na, or Mg atoms. Some of these molecules are dimers and weakly bound water complexes, which will test the ability of ccCA to properly model the energetics of long-range interactions, a common shortcoming of DFT methods. This training set also contains two rather large complexes—magnesocene [$Mg(C_5H_5)_2$] and beryllium bis(acetylacetonate) [$Be(C_5H_7O_2)_2$]—for which the calculation of theoretical ΔH_f values is likely intractable using large basis set coupled cluster techniques. In addition to the Cioslowski training set, we have included three extra *s*-block oxides and hydroxide compounds [Li_2O, $Be(OH)_2$, and $Mg(OH)_2$] where G*n* methods historically have failed. As a comparison, only 10 enthalpies of formation for molecules containing Li, Be, Na, or Mg were included in the G3/05 set of 454 energies.[28]

Computational Methods

Ab initio and DFT computations were carried out with the Gaussian03 software package.[42] Structures were optimized at the B3LYP level of theory with cc-pVTZ basis sets. Harmonic vibrational frequencies scaled by a factor of 0.9854 were also computed using B3LYP/cc-pVTZ at the equilibrium geometries to obtain the required zero-point vibrational energies (ZPVE) and temperature-dependent enthalpy corrections. Single-point MP2 energies were extrapolated to the CBS limit using a three-point mixed exponential/Gaussian formula (ccCA-P)[43]

$$E(x) = E_{CBS} + B\exp[-(x-1)] + C\exp[-(x-1)^2]$$

where $x = D, T, Q$ and is the cardinal number or zeta-level of the aug-cc-pV*x*Z basis sets, and the two-point (TQ) Schwartz inverse-power formula (ccCA-S4)[44−50]

$$E(l_{max}) = E_{CBS} + \frac{B}{\left(l_{max} + \frac{1}{2}\right)^4}$$

where l_{max} is the maximum angular momentum of the basis set (equivalent to *x* for first- and second-row atoms and molecules). Additive corrections to the MP2 energies to account for higher-order electron correlations, core−valence correlations, and treatment of scalar relativistic effects were then made using the standard ccCA formalism in ref 39. It is important to note that by using MP2 energies that have been extrapolated to the CBS limit, the BSSE should be eliminated. Thus, no counterpoise corrections should be necessary for a proper treatment of *s*-block molecules using ccCA. Newly optimized (aug)-cc-p(C)V*x*Z basis sets for Li, Be, Mg, and Na were obtained from Peterson et al.[51] For this study, a revised second-row core−valence basis set augmented with tight-*d* functions [aug-cc-pCV($x + d$)Z] has also been used.[52] For comparison, standard G3 energies[14] and G3B, sometimes referred to as G3B3 or G3(B3LYP)[53] (where B3LYP 6-31G(d) equilibrium geometries and harmonic vibrational frequencies are computed), were obtained for the 42 target complexes, and enthalpies of formation were computed in the manner outlined by Curtiss and co-workers.[15]

Results and Discussion

The G*n* benchmark sets (the most recent of which is the previously mentioned G3/05 set containing 454 energetic quantities) have a stringent criteria for inclusion: only molecules whose ΔH_f values have at most ± 1 kcal mol^{-1} in experimental uncertainty.[14,17,28] If new data cast doubt on the experimental value of a molecule within the G3/05 training set, it can be removed, as was the case for the ΔH_f value of COF_2.[17,54] The training set created by Cioslowski and co-workers relaxes this criterion somewhat, including molecules with uncertainties of up to ± 5.0 kcal mol^{-1}. For the G3/99 test set of 376 compounds, the G3 model chemistry has a mean absolute deviation (MAD) of 1.16 kcal mol^{-1}, while ccCA-S4 and ccCA-P have a MAD of 0.96 and 0.97 kcal mol^{-1}, respectively.[39] Gas-phase enthalpies of formation (ΔH_f) at 298.15 K using ccCA-S4, ccCA-P, G3, and G3B are given in Table 1 along with experimental values and corresponding uncertainties. As expected, the ccCA-P and ccCA-S4 enthalpies of formation generally agree with one another to within a few tenths of a kilocalorie per mole. The differences in ccCA-P and ccCA-S4 enthalpies of formation increase with molecular size. As ccCA-S4 performs better, with a 1.0 kcal mol^{-1} improvement for $Be(acac)_2$ and a 0.8 kcal mol^{-1} improvement for $Mg(C_5H_5)_2$, ccCA-S4 appears to be slightly more reliable than ccCA-P for the *s*-block systems, and our discussion will focus on the ccCA-S4 results.

For the 42 *s*-block complexes studied, both of the preferred ccCA model chemistries have a mean signed deviation (MSD) of 0.05 kcal mol^{-1}, showing almost no systematic bias with regard to the experimental ΔH_f values. On the other hand, the G3 MSD is -0.88 kcal mol^{-1}, suggesting that the G3 method predicts ΔH_f values for *s*-block molecules that are systematically too high. This is quite surprising, as the G3 HLC is optimized to have a near-zero MSD for the G3/99 training set. The G3B MSD of -0.15 kcal mol^{-1} implies a smaller bias. It is important to mention that the ccCA implementations used in this study also have a near-zero MSD for the G3/99 set, but without any

TABLE 1: Computed Gas-Phase Enthalpies of Formation (298.15 K) in kcal mol^{-1} with ccCA and G3 Composite Methods

molecule	ccCA-P	deviation	ccCA-S4	deviation	G3	deviation	G3B	deviation	expt[a]	σ
$(BeF)_2O$	−292.9	5.0	−293.2	5.3	−288.1	0.2	−290.4	2.5	−287.9	5.0
$Be(acac)_2$	−268.9	−3.8	−269.9	−2.8	−271.7	−1.0	−271.3	−1.4	−272.7	0.7
$BeCl_2$	−86.6	0.5	−86.5	0.4	−83.4	−2.7	−85.1	−1.0	−86.1	2.5
BeCl	15.4	−0.9	15.4	−0.9	17.8	−3.3	16.8	−2.3	14.5	3.0
BeF_2	−191.0	0.7	−191.1	0.8	−187.2	−3.1	−188.8	−1.5	−190.3	1.0
BeF	−39.6	−1.0	−39.7	−0.9	−36.9	−3.7	−37.9	−2.7	−40.6	2.0
BeH	81.1	0.6	81.1	0.6	82.2	−0.5	82.0	−0.3	81.7	n/a
BeO	30.5	2.1	30.5	2.1	38.5	−5.9	37.7	−5.1	32.6	2.9
$Be(OH)_2$	−151.5	0.4	−151.7	0.6	−147.8	−3.3	−148.6	−2.5	−151.1[b]	1.7
$(LiCl)_2$	−142.4	−0.7	−142.3	−0.8	−141.5	−1.6	−143.3	0.2	−143.1	3.0
Li_2	50.5	1.1	50.5	1.1	49.4	2.2	49.2	2.4	51.6	0.7
Li_2O	−38.4	2.5	−38.4	2.5	−35.0	−0.9	−35.7	−0.2	−35.9[b]	1.0
$(LiOH)_2$	−177.9	1.8	−177.7	1.6	−177.2	1.1	−178.0	1.9	−176.1	2.4
$(LiCl)_3$	−229.1	−11.0	−228.9	−11.2	−229.4	−10.7	−232.1	−8.0	−240.1	5.0
LiF	−82.1	2.0	−82.0	1.9	−80.4	0.3	−81.3	1.2	−80.1	n/a
LiH	32.4	0.9	32.4	0.9	33.0	0.3	32.9	0.4	33.3	n/a
LiNa	41.9	1.5	41.9	1.5	40.1	3.3	39.8	3.6	43.4	0.3
LiOH	−58.3	3.6	−58.2	3.5	−56.6	1.9	−57.0	2.3	−54.7	1.2
$Mg(C_5H_5)_2$	34.1	−1.2	33.3	−0.4	31.8	1.1	32.8	0.1	32.9	0.9
$MgCl_2$	−94.3	0.5	−94.2	0.4	−92.6	−1.2	−94.4	0.6	−93.8	0.5
MgF_2	−174.3	0.6	−174.1	0.4	−173.3	−0.4	−175.1	1.4	−173.7	4.0
MgF	−51.2	−5.4	−51.1	−5.5	−50.7	−5.9	−51.7	−4.9	−56.6	2.0
MgO	32.4	3.6	32.5	3.5	36.5	−0.5	35.6	0.4	36	5.0
$Mg(OH)_2^-$	−132.0	1.3	−131.9	1.2	−129.2	−1.5	−130.1	−0.6	−130.7[b]	1.0
$MgOH^+$	141.1	4.9	141.2	4.8	144.1	1.9	143.6	2.4	146	5.0
Na_2^+	146.0	0.7	146.0	0.7	144.4	2.3	144.3	2.4	146.7	0.3
$(NaCl)_2$	−134.2	−1.1	−134.0	−1.3	−138.3	3.0	−140.1	4.8	−135.3	2.0
$(NaF)_2$	−196.0	−6.3	−195.8	−6.5	−202.6	0.3	−204.4	2.1	−202.3	3.0
Na_2	32.8	1.2	32.7	1.3	30.0	4.0	29.7	4.3	34	0.3
Na_2O	−6.6	−2.0	−6.5	−2.1	9.8	−18.3	8.8	−17.4	−8.6	1.9
NaCl	−43.2	−0.4	−43.1	−0.5	−44.0	0.4	−44.9	1.3	−43.6	n/a
NaCN	29.5	−7.0	29.5	−7.0	28.6	−6.1	27.6	−5.1	22.5	0.5
NaF	−69.7	0.3	−69.7	0.3	−70.2	0.8	−71.1	1.7	−69.4	0.5
$Na(H_2O)^+$	61.3	1.1	61.3	1.1	62.0	0.4	62.4	0.3	62.4	n/a
$Na(H_2O)_2^+$	−17.0	1.8	−17.0	1.8	−16.4	1.2	−16.2	1.0	−15.2	n/a
$Na(H_2O)_3^+$	−92.0	3.2	−92.0	3.2	−91.6	2.8	−91.4	2.6	−88.8	n/a
$Na(H_2O)_4^+$	−164.1	3.7	−164.0	3.6	−164.3	3.9	−164.0	3.6	−160.4	n/a
NaH	32.6	−2.9	32.6	−2.9	32.1	−2.4	32.0	−2.3	29.7	4.6
$Na(NH_3)^+$	105.2	−1.1	105.2	−1.1	105.7	−1.6	106.4[c]	−2.3	104.1	0.5
NaO	21.3	−0.5	21.4	−0.6	20.1	0.7	19.2	1.6	20.8	1.0
$(NaOH)_2$	−150.4	1.3	−150.2	1.1	−154.0	4.9	−154.9	5.8	−149.1	2.4
NaOH	−46.1	0.4	−46.1	0.4	−45.8	0.1	−46.3	0.6	−45.7	1.9
MSE		0.0		0.0		−0.9		−0.1		
MAD		2.2		2.2		2.7		2.6		

[a] Exptl values and uncertainties are taken from ref 41 and references therein unless noted. [b] Reference 24. [c] The G3B ΔH_f value for NaOH was obtained using linear equilibrium geometry, even though the B3LYP/6-31G(d) potential energy surface spuriously predicts a bent equilibrium geometry.

HLC. The fact that ccCA deviations are close to zero for a training set with dramatically different bonding situations than the G3/99 set is a promising indicator that ccCA, in spite of being a more expensive composite approach, could be more universally reliable across the periodic table than G*n* methods.

Overall, the two implementations of ccCA used in this study are an improvement over G3 and G3B, and each ccCA implementation has a MAD of 2.2 kcal mol^{-1} versus 2.7 kcal mol^{-1} using G3 and 2.6 kcal mol^{-1} using G3B. While the average errors for both families of model chemistry are quite large as compared to their MADs for the G3/99 training sets, cognizance must be taken of the fact that the experimental uncertainties in this test set can be up to 5 kcal mol^{-1}. These experimental uncertainties may also prove to be conservative, as experimental thermochemical studies of *s*-block compounds are very challenging due to high reactivity in the gas phase.[55] For example, the ΔH_f value of MgO used by Cioslowski (36.0 ± 5.0 kcal mol^{-1}) comes from a 1989 study by Operti and co-workers,[56] while other experimental values for MgO range from 4.1 to 36.1 kcal mol^{-1}.[24] The recommended value based on theoretical computations from Sullivan and co-workers[24] is quite a bit lower, 33.9 ± 2.4 kcal mol^{-1}. The value recommended by Sullivan et al. is in good agreement with ccCA results (32.4−32.5 kcal mol^{-1}), but the G3 and G3B values (36.5 and 35.6 kcal mol^{-1}, respectively) are significantly too high.

In Figure 1, a histogram of signed deviations is shown for the 42 *s*-block molecules. Of the 42 molecules, the G3 method is chemically accurate using the stringent *p*-block criterion (i.e., has deviations less than ±1.0 kcal mol^{-1}) for 19 systems versus 16 systems with ccCA-S4.[41] In regards to chemical accuracy, G3B actually performs worse than the other three model chemistries, with only 11 of the 42 molecules within ±1.0 kcal mol^{-1} of the experimental value. However, as in the case of MgO, where ccCA is closer to a different recommended value than G3, the overall uncertainties of the training set must be kept in mind. For all of the systems in this investigation where experimental uncertainties (σ) are quoted, the average σ value is ±2.05 kcal mol^{-1}. Considering this σ for our entire training set, 27 of 42 molecules are within this range with ccCA-S4 versus 23 molecules with G3 and 20 molecules with G3B. As eight of the systems investigated have no error bars associated with their experimental ΔH_f value, 84% of the remaining 32 ccCA values is within the average experimental σ, as compared to 72% using G3 and 63% using G3B. The G3 and G3B

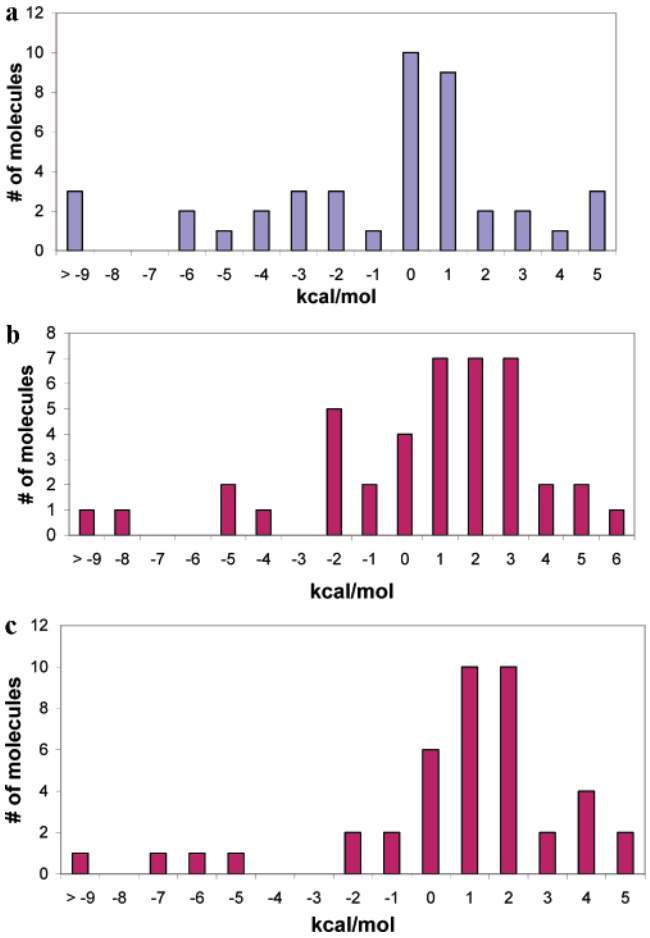

Figure 1. Histogram corresponding to the range of deviations for the 42 *s*-block molecules in the Cioslowski test set using (a) G3, (b) G3B (or G3B3), and (c) ccCA-S4 model chemistries.

methods also each predict five molecules with an absolute deviation greater than ±5.0 kcal mol^{-1}: BeO, $(LiCl)_3$, MgF (with G3), Na_2O (with G3B), and NaCN. Only four molecules have deviations greater than ±5.0 kcal mol^{-1} with ccCA implementations: $(BeF)_2O$, $(LiCl)_3$, $(NaF)_2$, and NaCN.

Of the 34 molecules in the 42 molecule set that have reported uncertainties in their experimental ΔH_f values, there are only 11 molecules for which G3 ΔH_f values are within the error bars, as compared to 14 moleclues using G3B and 19 molecules for ccCA-S4. The lithium chloride trimer, MgF, and NaCN[57] are molecules for which both ccCA and G3 methods have a similar ΔH_f value but significantly deviate from reported experimental values. The gas-phase enthalpies of formation for these molecules should be revisited with experimental techniques or perhaps yet more sophisticated theoretical investigations.

Calculation of the $Be(acac)_2$ enthalpy of formation is the largest ccCA computation to date. With D_{2d} Abelian point group symmetry, the $Be(acac)_2$ MP2/aug-cc-pVQZ single point contains 1936 basis functions, and the CCSD(T)/cc-pVTZ single point contains 674 basis functions. These additive ccCA computations were run on a single-node SMP machine with 8 DualCore AMD Opteron 885 processors and 16 gigabytes of RAM. The computation of the MP2 aug-cc-pVQZ energy required 71 h of computing time and 1.42 terabytes of disk space, while the CCSD(T) cc-pVTZ single point required 438.5 h of computing time (or 18.25 days) and 930 gigabytes of disk space. To use ccCA to routinely address systems of a more substantial size than $Be(acac)_2$, which has 29 atoms (15 non-hydrogen), further improvements in methodology/coding will be of use and are currently under investigation in our laboratories.

Conclusion

A preliminary study of the ccCA model chemistry for *s*-block metal oxides and hydroxides was expanded to 42 complexes and includes a variety of ligands and bonding types. While G*n* methods have difficulty describing core−valence correlation effects between M−O bonds without modification of the model chemistry, this difficulty is not universal, and G3/G3B perform well for many metal−halogen bonded systems as well as hydrated sodium ions. Overall, though, the ccCA outperforms G3 for the 42 molecules investigated, with a MAD of 2.2 kcal mol^{-1} versus 2.7 kcal mol^{-1} for G3 and 2.6 kcal mol^{-1} for G3B. Unlike the G3 model chemistry, the ccCA implementations used in this study have an almost zero MSE, suggesting less systematic error among the ccCA ΔH_f values. The G3, G3B, and ccCA methods have similar enthalpies of formation for $(LiCl)_3$, MgF, and NaCN, yet these values are significantly outside of the quoted experimental uncertainties. The ΔH_f values of these three molecules may benefit from future experimental and theoretical validation to determine if the error lies with the model chemistries or the experimental value.

The molecule $Be(acac)_2$ represents the largest molecule to date computed using ccCA model chemistry. Although the CCSD(T)/cc-pVTZ single-point energy for this molecule was extremely expensive, even larger molecules would be computationally tractable with the ccCA method if a software package optimized for large scale parallelization was employed. Thus far, application of the ccCA model chemistry to over 425 *s*- and *p*-block compounds has resulted in no remarkable failures. ccCA is a black box composite method useful for computing accurate energies of molecules that have a large diversity in size, atomic composition, and bonding type.

Acknowledgment. CASCaM is supported by a grant from the United States Department of Education. This research is partially supported by a grant from the United States Department of Energy, Office of Basic Energy Sciences (T.R.C.), Grant DE-FG02-03ER15387, and by a National Science Foundation CAREER Award CHE-0239555 (A.K.W.). Additional support was also provided by the University of North Texas Academic Computing Services for the use of the UNT Research Cluster. Computations employed the UNT computational chemistry resource, whose purchase was supported by a CRIF grant from the U.S. National Science Foundation (CHE-0342824). Some computations were supported by the National Computational Science Alliance under CHE010021 and utilized the SGI Altix. Prof. Kirk A. Peterson (Department of Chemistry, Washington State University) is thanked for providing new Group IA/IIA correlation consistent basis sets prior to their publication. Group IA/IIA correlation consistent basis sets are available upon request (kipeters@wsu.edu). Brian P. Prascher assisted by constructing Group IA/IIA Douglas−Kroll relativistic basis sets. The aug-cc-pCV(x + d)Z and Douglas−Kroll basis sets are also available upon request (akwilson@unt.edu). D.S.H. is a student at the Texas Academy of Mathematics and Sciences (TAMS) and has been supported by a TAMS Summer Fellowship.

References and Notes

(1) Edwards, S. J.; Freeman, C. G.; McEwan, M. J.; Wilson, P. F. *Int. J. Mass Spectrom.* **2006**, *255*, 164.

(2) Mó, O.; Yáñez, M.; Gal, J. F.; Maria, P. C.; Decouzon, M. *Chem.—Eur. J.* **2003**, *9*, 4330.
(3) Gal, J. F.; Maria, P. C.; Mó, O.; Yáñez, M.; Kuck, D. *Chem.—Eur. J.* **2006**, *12*, 7676.
(4) Gal, J. F.; Maria, P. C.; Decouzon, M.; Mó, O.; Yáñez, M.; Abboud, J. L. M. *J. Am. Chem. Soc. B* **2003**, *125*, 10394.
(5) Petrie, S. *Int. J. Mass Spectrom.* **2006**, *254*, 136.
(6) Plane, J. M. C. *Chem. Rev.* **2003**, *103*, 4963.
(7) Antony, J.; Grimme, S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5287.
(8) Hsueh, M. L.; Ko, B. T.; Athar, T.; Lin, C. C.; Wu, T. M.; Hsu, S. F. *Organometallics* **2006**, *25*, 4144.
(9) Gong, Z.; Shen, H. Y.; Zhu, W. L.; Luo, X. M.; Chen, K. X.; Jiang, H. L. *Chem. Phys. Lett.* **2006**, *423*, 339.
(10) Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkley, J. S. *J. Chem. Phys.* **1985**, *89*, 2198.
(11) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.
(12) Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537.
(13) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
(14) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
(15) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.
(16) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *J. Chem. Phys.* **1997**, *106*, 6764.
(17) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys*. **2000**, *112*, 7374.
(18) Raghavachari, K.; Curtiss, L. A. Evaluation of Bond Energies to Chemical Accuracy by Quantum Chemical Techniques. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific Press: Singapore, 1995; Vol. II, p 991.
(19) Curtiss, L. A.; Redfern, P. C.; Frurip, D. J. Theoretical Methods for Computing Enthalpies of Formation of Gaseous Compounds. In *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15, p 147.
(20) Haworth, N. L.; Sullivan, M. B.; Wilson, A. K.; Martin, J. M. L.; Radom, L. *J. Phys. Chem. A* **2005**, *109*, 9156.
(21) Radom, L.; Sullivan, M. B.; Haworth, N. L.; Wilson, A. K.; Curtiss, L. A.; Martin, J. M. *Abstr. Pap. Am. Chem. Soc.* **2004**, *228*, 533.
(22) Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 6014.
(23) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.
(24) 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.
(25) Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129.
(26) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*.
(27) Curtiss, L. A.; Raghavachari, K. *Theor. Chem. Acc.* **2002**, *108*, 61.
(28) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2005**, *123*, 124017.
(29) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys*. **2001**, *114*, 108.
(30) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 6138.
(31) Petrie, S. *Chem. Phys. Lett.* **1998**, *283*, 131.
(32) Schulz, A.; Smith, B. J.; Radom, L. *J. Phys. Chem. A* **1999**, *103*, 7522.
(33) Ma, N. L.; Siu, F. M.; Tsang, C. W. *Chem. Phys. Lett*. **2000**, *322*, 65.
(34) Petrie, S. *J. Phys. Chem. A* **2001**, *105*, 9931.
(35) Abirami, S.; Ma, N. L.; Goh, N. K. *Chem. Phys. Lett.* **2002**, *359*, 500.
(36) Siu, F. M.; Ma, N. L.; Tsang, C. W. *J. Chem. Phys.* **2001**, *114*, 7045.
(37) DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2006**, *124*, 114104.
(38) DeYonker, N. J.; Cundari, T. R.; Wilson, A. K.; Sood, C. A.; Magers, D. H. *THEOCHEM* **2006**, *775*, 77.
(39) DeYonker, N. J.; Grimes, T.; Yockel, S.; Dinescu, A.; Mintz, B.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2006**, *125*, 104111.
(40) Ho, D. S.; DeYonker, N. J.; Wilson, A. K.; Cundari, T. R. *J. Phys. Chem. A* **2006**, *110*, 9767.
(41) Cioslowski, J.; Schimeczek, M.; Liu, G.; Stoyanov, V. *J. Chem. Phys*. **2000**, *113*, 9377.
(42) 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 C.02; Gaussian, Inc.: Pittsburgh, PA, 2004.
(43) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.
(44) Schwartz, C. *Phys. Rev. A* **1962**, *126*, 1015.
(45) Schwartz, C. Estimating Convergence Rates of Variational Calculations. In *Methods in Computational Physics*; Alder, B. J., Fernbach, S., Rotenberg, M., Eds.; Academic Press: New York, 1963; Vol. 2, p 262.
(46) Kutzelnigg, W.; Morgan, J. D. *J. Chem. Phys.* **1992**, *96*, 4484.
(47) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.
(48) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys*. **1997**, *106*, 9639.
(49) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 136.
(50) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.
(51) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr., unpublished work.
(52) Yockel, S.; Wilson, A. K. *Theor. Chem. Acc.* **2007**, in press.
(53) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.
(54) Asher, R. L.; Appelman, E. H.; Ruscic, B. *J. Chem. Phys.* **1996**, *105*, 9781.
(55) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl. No. 1* **1988**, *17*.
(56) Operti, L.; Tews, E. C.; MacMahon, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 9152.
(57) Value of $\Delta H_{f(g)}$ given for NaCN in the JANAF tables, which is the value used by Cioslowski et al.,[41] is measured at 800−1350 K and presumes a linear structure at room temperature/0 K (vs the bent or t-shaped structure found by ccCA and G3 geometry optimizations.) This is suggested as a possible source for the discrepancy among theoretical enthalpies of formation and tabulated values for this molecule.