Performance of the correlation-consistent composite approach for sulfur species

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The performance of the correlation-consistent composite approach (ccCA) model chemistry has been examined for a test set of sulfur-containing molecules which includes enthalpies of formation, bond dissociation enthalpies (BDEs), and isomerization energies. The ccCA method was compared with other model chemistries (G3, G3B3) and, overall, was found to be more accurate than both G3 and G3B3 for sulfur-containing species, and at a moderate increase in computational cost. The ccCA model chemistry resulted in a mean absolute deviation (MAD) of 3.6 kJ/mol for the enthalpy of formation test set as compared with 8.3 and 9.6 kJ/mol for G3 and G3B3, respectively. The 95% confidence interval in the enthalpies of formation, which corresponds to two times the root mean square of the deviation from experiment, for the ccCA model chemistry is ± 10.3 kJ/mol as compared with ± 23.2 and ± 27.5 kJ/mol for the G3 and G3B3 methods. For the BDEs, the MAD for ccCA is 2.6 kJ/mol as compared with 4.4 and 4.3 kJ/mol for G3 and G3B3, respectively. The 95% confidence interval for BDEs for the ccCA model chemistry is ± 7.0 kJ/mol as compared with ± 10.3 and ± 10.1 kJ/mol for G3 and G3B3, respectively. Three isomeric systems which have resulted in disagreement among prior theoretical studies, NSO/SNO, HOS/HSO, and FSSF/SSF$_2$, were also examined using ccCA, and, in each case, ccCA correctly predicted the lowest isomer and agreed within 4 kJ/mol of previously reported values.

Keywords: Ab initio, composite approaches, ccCA, thermochemistry

1. Introduction

There is a tremendous need to accurately predict thermodynamic and kinetic properties of sulfur species in atmospheric, biological, industrial, and interstellar processes. Whether it be the SO_x processes responsible for large amounts of acid precipitation in the Northern Hemisphere (*1*) or detecting CS, OCS, H$_2$S, and other small sulfur-containing species in interstellar comets (*2*), numerous problems arise when trying to accurately model such systems. Impurities and side reactions can plague experimental work due largely to the instability of these gaseous molecules. Errors are not only limited to laboratory-related experimental uncertainties (uniformly expressed in experimental thermochemistry as the best estimate of the 95% confidence interval), but additionally, problems have been discovered in large compendiums of thermochemical data, such as the JANAF tables. For example, Lodders recently discovered four errors due to incorrect conversion

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data entry for sulfur-containing molecules as reported in the third and fourth edition of the JANAF tables, specifically for the molecules HS(g), S_2O(g), NS(g), and PS(g) (*3*).

Computational chemistry has become one of the most powerful aids for predicting accurate structural and energetic properties for sulfur species, especially for small molecules (*4–10*). However, despite this, there have been a number of challenges inherent in the computational study of sulfur-containing systems. In particular, sulfur species have shown sensitivity to basis set construction and basis set choice, as evidenced by numerous examples in the literature (*11–20*). To illustrate, in the 1990s, a deficiency was noted in the correlation-consistent basis sets, which are known for their utility in predicting accurate molecular and energetic properties. These sets (cc-pVnZ where n = D,T,Q, etc.), first introduced by Dunning in 1989 (*21*), were designed in such a way that as the basis set quality is increased, the energy or property of interest converges toward a limit. This limit, which can be obtained by extrapolation of the calculated data, is called the complete basis set (CBS) limit, the limit at which no further improvement of the basis set can improve upon the property description. When paired with methodology such as the coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)], the CBS limit obtained utilizing the correlation-consistent basis sets is known to provide 'chemical accuracy' (± 4 kJ/mol from reliable experiment) in energetic properties, particularly for small, main group species, although additional corrections (*e.g.* core-valence correlation, spin-orbit coupling, etc.) must often be taken into account to reach this level of accuracy. (Chemical accuracy is generally considered to be ± 4 kJ/mol and is similar in definition to experimental uncertainty in that it should give a best estimate of the 95% confidence interval of the methodology.) Thus, the 25 kJ/mol error in the CCSD(T)/CBS binding energy for SO_2 reported in 1995 by Bauschlicher and Partridge was quite surprising (*13*) and pointed to a possible deficiency in the original formulation of the correlation-consistent basis sets for sulfur. They noted a substantial decrease in this error by adding tight (high exponent) d functions to the sulfur basis sets (*13, 14*). Studies by Martin and coworker (*15, 22*) suggested the necessity of additional tight functions in the correlation-consistent basis sets for not only sulfur, but also for all second-row atoms, and they considered adding not only d functions, but also additional higher angular momentum functions (d, f, g) as well.

These findings led Dunning *et al.* to re-examine the second-row correlation-consistent basis sets for aluminum through argon (*23*). In this study, they noted deficiencies in the description of the sets, and developed revised sets, preserving the essential systematic behaviour of the sets upon increasing basis set size. (The challenge of basis set development is that the addition of any function to the basis set will improve the total energy, but, unfortunately, arbitrary additions to a basis set will ruin the systematic behaviour needed to provide accurate extrapolations toward the CBS limit.) These revised basis sets are denoted cc-pV($n + d$)Z (where n = D, T, Q, or 5) to indicate the inclusion of one tight d function (*23*). The modified basis set only slightly increases the computational demands of the calculation. Numerous studies have been carried out utilizing these modified basis sets in combination with methods such as the second-order Møller–Plesset perturbation (MP2) theory, CCSD(T), and several varieties of the density functional theory (DFT) (*18–20*). These prior studies have demonstrated the importance of the cc-pV($n + d$)Z basis sets in calculations on second-row species to achieve improved accuracy and correct convergence behaviour to the CBS limit of energetic properties as the size of the basis set is increased.

To achieve 'chemical accuracy' (± 4 kJ/mol at a 95% confidence rate from a reliable experiment) in energetic properties (*e.g.* enthalpies of formation, ionization energies, and dissociation energies) for even small molecules, methods such as CCSD(T) in combination with large correlation-consistent basis sets are required. Unfortunately, such calculations become costly in terms of computer time, memory, and disk space requirements. Some of the most powerful alternatives to computationally demanding methods such as these have been composite approaches such as the Gn methods (*24–29*), the Wn methods (*17, 30–32*), the CBS-n methods (*33–38*), and more recently the

correlation-consistent composite approach (ccCA) (*39–43*). The goal of any composite approach is to reproduce accurate results such as those that can be obtained with CCSD(T) and a large basis set, but at a reduced computational cost. Generally speaking, the formalism for any composite method depends primarily upon the overall accuracy which the users require, and that desired accuracy determines the model chemistry that is most appropriate. In the most extreme case, the W4 theory, the goal for accuracy of energetic properties is sub-kJ/mol, but this comes at a very large computational cost (*32*). The current implementation of ccCA has demonstrated a 95% confidence interval of approximately ± 10 kJ/mol for main group species (*39, 40*). In the case of ccCA, the desired accuracy for the method is an average error of ~ 4 kJ/mol for main group species, but at a computational cost resembling that of MP2 calculations (*39*). Therefore, ccCA is viable for larger systems, and calculations are on going in our laboratory with molecules as large as C_{60}.

Numerous sulfur studies have been performed in the past with model methods such as the G*n* methods on molecules such as SF_x, CH_3SO_XH, and other small compounds (*5, 8, 44*). Although the G*n* methods have been shown to provide accurate thermodynamic data for sulfur species (*5*), these methods are wholly dependent upon an empirical correction (called the higher level correction, or HLC) for accuracy (*40*). As the HLC is dependent upon the number of electrons in the system, the factor grows substantially with respect to increasing system size. To illustrate, for the enthalpy of formation of linear alkanes, the HLC for G3B3 increases linearly as the size of the alkane chain is increased from methane to *n*-octane. For *n*-butane, the HLC is 87.5 kJ/mol and for *n*-octane, the HLC is over 200 kJ/mol (*39*). This is substantial, considering a target accuracy of ± 4 kJ/mol. The ccCA method is able to achieve similar (or better) accuracies than the G3B3 and G3 methods, without the inclusion of empirical factors such as the HLC.

In this work, the ccCA method is benchmarked against a wide variety of properties for sulfur-containing species including enthalpies of formation (ΔH_f°) and for the first time, bond dissociation enthalpies (BDEs). Additional calculations on sulfur species are performed where no clear consensus or experimental data are available in an effort to aid in the discussion.

2. Computational details

In the ccCA formalism, geometry optimizations and frequency calculations are carried out utilizing the B3LYP density functional in combination with the cc-pVTZ basis set (denoted as B3LYP/cc-pVTZ). At this geometry, a series of three single-point MP2 calculations are performed, utilizing the correlation-consistent basis sets (cc-pV*n*Z, where $n =$ D, T, and Q). The resulting energies are extrapolated to the CBS limit using the Peterson extrapolation (*45*):

$$E(n) = E(\infty) + B \exp^{-(n-1)} + C \exp^{-(n-1)^2} \tag{1}$$

where *n* is the cardinal number (cc-pVDZ = 2, cc-pVTZ = 3, etc.), $E(n)$ the energy utilizing the corresponding cc-pV*n*Z basis set, $E(\infty)$ the energy at the CBS limit, and both *B* and *C* are extrapolation parameters. A second extrapolation scheme, the two-point Schwartz-type fit (*46–48*), has also been successfully utilized for the ccCA methodology, and utilizes the MP2/cc-pVTZ and MP2/cc-pVQZ energies:

$$E(n) = E(\infty) + B \left(l_{max} + \frac{1}{2} \right)^{-4} \tag{2}$$

where l_{max} is the highest angular function for the basis set (*e.g.* for the cc-pVTZ basis set, $n = l_{max} = 3$ for main group species). The MP2 CBS limit energy, which can be expressed as

MP2/cc-pV∞Z, serves as the reference energy for the ccCA calculations. When ccCA utilizes Equation (1) for the extrapolation, the approach is referred to as the ccCA-P scheme, whereas for Equation (2), the approach is referred to as the ccCA-S scheme.

A number of terms are included additively to the reference energy, including factors which help to account for higher-level [ΔE(CC)], core-valence [ΔE(CV)], relativistic [ΔE(R)], spin-orbit [ΔE(SO)], and zero-point (ZPVE) energy effects. The ccCA expression is:

$$E(MP2/aug\text{-}cc\text{-}pV\infty Z) + \Delta E(CC) + \Delta E(CV) + \Delta E(R) + \Delta E(SO) + ZPVE \qquad (3)$$

where the ZPVE is determined from a B3LYP/cc-pVTZ calculation, and the appropriate ZPVE scaling is applied. The other terms are defined as follows:

$$\Delta E(CC) = E(CCSD(T)/cc\text{-}pVTZ) - E(MP2/cc\text{-}pVTZ) \qquad (4)$$

$$\Delta E(CV) = E(MP2(full)/aug\text{-}cc\text{-}pCVTZ) - E(MP2/cc\text{-}pVTZ) \qquad (5)$$

$$\Delta E(R) = E(MP2(DK)aug\text{-}cc\text{-}pVTZ\text{-}DK) - E(MP2/cc\text{-}pVTZ). \qquad (6)$$

The spin-orbit correction [ΔE(SO)] has been applied to the energies using the data from reference (*49*) for the atoms. Experimental spin-orbit effects for molecules, however, have not been included in this test set due to the lack of experimental values for all of the molecules within this set. It must be noted that spin-orbit effects can be quite large for second-row systems such as SF (4.63 kJ/mol) (*50*). The ccCA methodology, as outlined above, has been successfully used to predict over 1000 energetics to date (*39–43*).

To provide contrast to ccCA, G3 is based upon MP2/6-31G(d) geometries and UHF/6-31G(d) frequencies, whereas the G3B3 composite approach uses B3LYP/6-31G(d) geometries and frequency calculations, (*51*) similar to ccCA. While G3 and G3B3 use a reference energy of MP4/6-31G(d), the ccCA formalism uses a reference energy of MP2/aug-cc-pV∞Z. In addition, the G3 and G3B3 schemes include a 'higher-level correction' term, an empirical factor, which can become substantially large, and is based upon fits to well-established experimental data, as described further in reference (*51*). ccCA does not include this empirical factor. Further additive corrections are added to the reference energies for both composite approaches and a more detailed comparison can be found in reference (*40*).

A benchmark test set was also constructed based upon 40 experimental enthalpies of formation [$\Delta H_{\mathrm{f}}^{\circ}$ (298.15 K)] for a number of sulfur species, including sulfur in various bonding environments (Table 1). As the average deviation from experiment for ccCA has been shown in earlier studies to be ~4.0 kJ/mol for thermodynamic properties and therefore the 95% confidence interval is ±10 kJ/mol, the benchmark species were selected so that no single species has an uncertainty > 10 kJ/mol. Further comparisons include BDEs as well as isomerization energies of several molecules for which theoretical results have not been in agreement (*e.g.* FSSF versus SSF$_2$).

All G3, G3B3, and ccCA calculations were carried out utilizing the G03 program package (*52*). For correct convergence and accuracy in second-row systems, the inclusion of a tight-*d* function in the basis set is necessary, and therefore, for all ccCA calculations, the '*n*' was replaced by '*n + d*' varieties of all families of the correlation-consistent basis sets for sulfur, in each step of the ccCA calculations (*e.g.* aug-cc-pVTZ was replaced by aug-cc-pV(T + *d*)Z, cc-pCVTZ was replaced by cc-pCV(T + *d*)Z, and so on).

Table 1. Enthalpy of formation (ΔH_f°) and deviation from experiment [$\Delta(\Delta H_f^\circ)$] at 298.15 K for 40 sulfur-containing molecules reported in kJ/mol. All experimental values found in references (58), (81), or (82) unless otherwise indicated[†].

	ΔH_f°						$\Delta(\Delta H_f^\circ)$			
	ccCA-P	ccCA-S4	G3	G3B3	Expt.	Uncert.[‡]	ccCA-P	ccCA-S4	G3	G3B3
cyclo-CH$_2$CH$_2$CH$_2$S	64.2	62.8	65.6[§]	66.9	61.1	1.3	3.1	1.7	4.5	5.8
CH$_2$S	117.5	117.3	115.6[¶]	115.5	114.7	8	2.8	2.6	0.9	0.8
(CH$_3$)$_2$CHSH	−76.3	−77.9	−76.1[¶]	−74.4	−76.94	0.63	0.6	−1.0	0.8	2.5
(CH$_3$)$_3$CSH	−108.6	−110.6	−111.6[¶]	−109.6	−108.74	0.88	0.1	−1.9	−2.9	−0.9
cyclo-CH$_3$CH$_2$CHS	43.8	42.5	44.0[¶]	45.2	46.11	2	−2.3	−3.6	−2.1	−0.9
CH$_3$CH$_2$CH$_2$SH	−65.9	−67.5	−64.6[¶]	−63.2	−68.58	0.63	2.7	1.1	4.0	5.4
CH$_3$CH$_2$SCH$_2$CH$_3$	−80.5	−82.8	−81.9	−79.4	−83.5	2.3	3.0	0.7	1.6	4.1
CH$_3$CH$_2$SCH$_3$	−59.3	−61.1	−58.9	−56.8	−60.3	1.1	1.0	−0.8	1.4	3.5
CH$_3$CH$_2$SH	−45.7	−46.9	−43.5[¶]	−42.4	−46.1	0.6	0.4	−0.8	2.6	3.7
CH$_3$OSOOCH$_3$	−473.7	−476.0	−465.6	−463.8	−483.25	2.09	9.6	7.3	17.7	19.5
CH$_3$S	123.6	122.9	122	122	124.6[#]	1.8	−1.0	−1.7	−2.6	−2.6
CH$_3$SCH$_3$	−38.1	−39.4	−35.9[¶]	−34.2	−37.5	2	−0.6	−1.9	1.6	3.3
CH$_3$SH	−24.3	−25.0	−20.7[¶]	−19.9	−22.84	0.59	−1.5	−2.2	2.1	2.9
CH$_3$SOOCH$_3$	−370.3	−372.6	−362.4	−358.5[‖]	−372.79	3.35	2.5	0.2	10.4	14.3
CH$_3$SOCH$_3$	−150.4	−152.3	−144.2	−141.4[‖]	−150.5	1.5	0.1	−1.8	6.3	9.1
CH$_3$SSCH$_3$	−24.9	−26.3	−19.8	−16.6	−24.1	2.3	−0.8	−2.2	4.3	7.5
ClS$_2$	66.1	66.1	67.6	72.6	78.6	8.4	−12.5	−12.5	−11.0	−6.0
ClSSCl	−24.5	−24.7	−17.2	−9.9	−16.74	4	−7.8	−8.0	−0.5	6.8
CS	280.2	280.5	276.0[§]	276.3	278.55	3.8	1.6	1.9	−2.6	−2.3
CS$_2$	112.1	112.4	103.8	105.2	116.7	0.84	−4.6	−4.3	−12.9	−11.5
H$_2$SO$_4$	−724.9	−726.5	−704.3	−702.5	−732.73	2	7.8	6.2	28.4	30.2
HBS	48.6	48.6	44.3	45.5	50.2	10	−1.6	−1.6	−5.9	−4.7
HOSO$_2$F	−738.5	−740.3	−726.9	−713.8	−753.12	8.4	14.6	12.8	26.2	39.3
NH$_2$CSNH$_2$	18.2	18.1	21.8	21.4	22.9	1.6	−4.7	−4.8	−1.1	−1.5
PS	168.9[¶¶]	169.2[¶¶]	166.3[§]	158.9	152.44[**]	10	16.5	16.8	13.9	6.5
S$_2$	129.7	129.9	132.2[§]	133.1	128.6	0.3	1.1	1.3	3.6	4.5
S$_2$O	−53.5	−53.7	−41.3	−43.4	−55.39[**]	1.1	1.9	1.7	14.1	12.0
SCl$_2$	−16.6	−16.9	−9.3	−3.9	−17.57	3.3	1.0	0.7	8.3	13.7
SCO	−142.9	−142.7	−149.7	−150.2	−141.7	2	−1.2	−1.0	−8.0	−8.5
SF	6.9	6.8	8.2[§]	9.8	12.97	6.3	−6.1	−6.2	−4.8	−3.2

(*Continued*)

Table 1. Continued.

	ΔH_f°						$\Delta(\Delta H_f^\circ)$			
	ccCA-P	ccCA-S4	G3	G3B3	Expt.	Uncert.[‡]	ccCA-P	ccCA-S4	G3	G3B3
SF$_2$	−294.1	−294.4	−282.8	−279.4	−289.3	6.2	−4.8	−5.1	6.5	9.9
SF$_6$	−1212.3	−1214.6	−1194.5	−1183.3	−1220.47	0.8	8.2	5.9	26.0	37.2
SH	142.9	142.8	141.1	141.2[∥]	142.92[**]	0.78	0.0	−0.1	−1.8	−1.7
SH$_2$	−23.9	−24.1	−18.8	−18.8[∥]	−20.502	0.8	−3.4	−3.6	1.7	1.7
SHCH$_2$CH$_2$SH	−5.2	−6.3	0.2	1.3	−9.33	1.09	4.1	3.0	9.5	10.6
SO	8.5	8.2	7.2[§]	6.1	5.01	1.3	3.5	3.2	2.2	1.1
SO$_2$	−296.0	−296.9	−280.9	−286.3[∥]	−296.81	0.2	0.8	−0.1	15.9	10.5
SO$_2$Cl$_2$	−346.5	−347.7	−336.6	−328.4	−354.8	2.1	8.3	7.1	18.2	26.4
SO$_2$F$_2$	−756.7	−758.6	−734.8	−730.7	−758.559	8.4	1.9	0.0	23.8	27.9
SO$_3$	−390.5	−391.7	−374.3	−377.4[∥]	−395.765	0.71	5.3	4.1	21.5	18.4
MAD[§§]							3.9	3.6	8.3	9.6
Std. Dev.							5.5	5.2	10.3	11.7
Thermo. Uncert.						1.8[‡‡]	11.0	10.3	23.2	27.5
Max. Dev.							16.5	16.8	28.4	39.3

[†]Two collections of experimental enthalpies of formation which were vital to the compilation of this data are references (*83*) and (*84*).
[‡]Thermochemical uncertainty corresponding to 95% confidence interval from experimental source.
[§]See reference (*54*). Previous G3 values are updated with more accurate atomic enthalpy of formation data.
[¶]See reference (*5*). Previous G3 values are updated with more accurate atomic enthalpy of formation data.
[∥]See reference (*44*). Previous G3B3 values are updated with more accurate atomic enthalpy of formation data.
[#]See reference (*85*).
[**]See reference (*3*).
[††]Thermochemical uncertainty defined as the 95% confidence interval for the benchmarked methods estimated by twice the root mean square.
[‡‡]Average of the reported experimental uncertainty.
[§§]Although MAD is the customary measure of fidelity for electronic structure methods, the MAD underestimates the thermochemical uncertainty by a factor of 2 and 3.
[¶¶]Utilizing a restricted open-shell formalism as opposed to a unrestricted formalism for PS results in values of 162.6 and 163.0 kJ/mol for ccCA-P and ccCA-S4, respectively.

3. Results and discussion

3.1. *Enthalpies of formation*

For the 40 $\Delta H_{\mathrm{f}}^{\circ}$ values in our test suite, the ccCA method shows improved accuracy over both the G3 and G3B3 methodology, as shown in Table 2. The mean absolute deviations (MADs) for ccCA-P and ccCA-S4 are 3.9 and 3.6 kJ/mol, respectively, similar to that shown previously for ccCA applied to the large G3/99 benchmark test set, 3.6 kJ/mol (*40*). The 95% confidence intervals, which correspond to two times the root mean square, are ±11.1 and ±10.3 kJ/mol, respectively, for ccCA-P and ccCA-S4. This leads to the conclusion that similar to what has been seen in previous main group studies for ccCA, the inverse quartic extrapolation scheme, Equation 2, provides slightly superior results than the mixed/Guassian exponential scheme, Equation 1. In the present study, the G3 and G3B3 methods result in MADs which are 8.3 and 9.6 kJ/mol, respectively, which is much larger than the MAD previously shown for G3 for the G3/99 test set, which was 4.4 kJ/mol (*53*). For a subset of the G3/99 test set, the G2/97 set, the MADs were 3.9 kJ/mol for both G3 and G3B3 (*51*). As compared with ccCA, both G3 and G3B3 have a much higher thermodynamic uncertainty, resulting in 95% confidence levels of ±23.2 and ±27.5 kJ/mol, respectively. In the original formulation of the G3B3 method, it was shown that one of the successes of the G3B3 method over G3 was for the sulfur-containing molecule SO_2 and that the use of the B3LYP geometries and frequencies in the SO_2 calculations reduced the overall error as compared with experiment by 5.4 kJ/mol (*51*). Interestingly, in the current study, although G3B3 results in improved accuracy for some sulfur-containing molecules, overall, it does far worse for the sulfur species than G3. In the worst cases, the use of the G3B3 method as compared with the G3 method increases the deviation from experiment for the SF_6 molecule from 26.0 to 37.2 kJ/mol and for $HOSO_2F$ from 26.2 to 39.3 kJ/mol. For SF_6, ccCA-P and ccCA-S4 resulted in deviations from the experiment of 8.2 and 5.9 kJ/mol, respectively, while for $HOSO_2F$, the deviations for ccCA-P and ccCA-S4 were 14.6 and 12.8 kJ/mol, respectively. For ccCA, the poorest performance is for the PS molecule (X $^2\Pi$). Both ccCA-P and ccCA-S4 underestimate the $\Delta H_{\mathrm{f}}^{\circ}$ by 16.5 and 16.8 kJ/mol, respectively. Previous CCSD(T)/CBS calculations by Denis (*54*) predicted a value for the enthalpy of formation of 159.6 ± 2.0 kJ/mol as compared with

Table 2.   Enthalpy of formation at 298.15 K calculated using the ccCA method for additional sulfur-containing molecules (kJ/mol). All experimental values are found in references (*58*) (*81*), or (*82*) unless otherwise indicated.

	Expt.	ccCA-P	ccCA-S4		Expt.	ccCA-P	ccCA-S4
AlS	238.5 ± 8.5	212.1	212.5	Na_2SO_4		−998.9	−1000.1
cyclo-CH_2CH_2S	82.38	77.4	76.5	$NaHSO_4$		−882.2	−883.7
CH_2SO		−32.4	−33.1	$NaSO_2$		−375.9	−376.3
CH_3CHS	50 ± 8	77.3	76.7	$NaSO_3$		−527.5	−528.5
CH_3CH_2S		101.3	100.2	$NaSO_3Cl$		−706.5	−707.7
CH_3OSO		−209.4	−210.7	NS	283.4 ± 24.0[†]	278.3	278.4
CH_3SO		−68.2	−69.3	NSO		179.9	179.4
CH_3SO_2		−212.5	−214.0	S_2F_2	−401.41 ± 41.8	−323.8	−324.1
CH_3SOO		90.1	89.4	SF_3	−503 ± 33.5	−358.8	−358.9
ClS	156.46 ± 16.7	120.2	120.1	SF_4	−763.16 ± 20.9	−769.2	−770.3
FSSF	−336.44 ± 41.8	−316.8	−316.9	SF_5	−908.45 ± 15.1	−845.6	−847.0
HOS		−7.3	−7.4	SF_5Cl	−1038 ± 10.5	−981.0	−983.0
$HOSO_2$		−369.5	−370.6	SNO		184.3	184.7
HSO		−21.5	−21.9	SO_2H_2		−236.3	−237.4
HSO_3		−183.5	−184.9	SO_4		−259.3	−261.1
HSOO		124.9	124.8	SOH_2		−286.9	−287.2
HSOOH		−41.6	−42.0	SON		411.3	411.5

[†]See reference (*3*).

the experimental value which was re-evaluated, based upon previous JANAF tables, by Lodders (*3*) (152.44 ± 10 kJ/mol). Although the values by Denis and Lodders are in good agreement, ccCA is not in agreement. This is most likely due to the occurrence of spin contamination and the lack of a multireference treatment. In the study by Denis (*54*), it was noted that for PS there was a large spin contamination of $S^2 = 1.0$ and that the T1 diagnostic was 0.033, suggesting a multireference procedure might be necessary. In light of these findings, a minor revision to the ccCA procedure, in which the unrestricted formalism was exchanged for a restricted formalism, was examined in order to gauge the effect of spin contamination in PS. Utilizing this procedure, the enthalpy of formation of PS was determined to be 162.6 and 163.0 kJ/mol for ccCA-P and ccCA-S4, respectively. These values are in good agreement with the previous CCSD(T)/CBS calculations by Denis (*54*).

Table 2 lists an additional set of molecules that do not have published experimental values, have experimental values that have been questioned, or have experimental uncertainties >10.0 kJ/mol. The values in Table 2 can be particularly helpful for estimating the ΔH_f° where no experimental values exist or highlighting the cases where experimental values may be in error. Two of the molecules, AlS and CH_3CHS, which have experimental uncertainties <10 kJ/mol, have resulted in substantial disagreement in previous studies. For the AlS molecule, previous CCSD(T) calculations at the CBS limit predict the enthalpy of formation to be 198.3 kJ/mol, which is 40 kJ/mol lower than that of the experiment (*54*). Other methods such as B3LYP and B3PW91 also result in comparable energies to the CCSD(T) calculations (*54*). The experimental ΔH_f° was determined in two different cases using mass spectrometric ion intensity data (*55, 56*) which produced values of 246.2 ± 8.2 and 231.1 ± 8.0 kJ/mol, respectively, utilizing the atomic enthalpy of formation data from the JANAF tables. For the JANAF tables, these values were then averaged to produce the tabulated value of 238.5 ± 8.5 kJ/mol. The reported value for AlS in the JANAF tables also utilized the thermodynamic value for Al(g), which has recently been questioned (*57*). In a study by Karton and Martin (*57*), the enthalpy of formation for Al(g) was predicted to be 8.1 kJ/mol higher in energy than the JANAF value. It would be highly informative if a new experimental study could be performed for AlS(g) as the raw data from the two mass spectrometry experiments were never published and therefore the current value was not reevaluated in the more recent JANAF tables (*58*).

For the CH_3CHS molecule, both ccCA-P and ccCA-S4 overestimate the ΔH_f° by 27.4 and 26.7 kJ/mol, respectively, well outside the experimental uncertainty of 8 kJ/mol for the ion cyclotron resonance spectroscopic experiment performed by Butler and Baer (*59*). The ΔH_f° at 298 K for CH_3CHS has been previously studied by Kieninger and Ventura (*60*) with the CBS-QB3 method using various isodesmic reactions and was also found to be significantly higher than the reported experimental result (67.8 versus 50.0 kJ/mol). They suggested that the reason for this large deviation from the experiment could be attributed to the fact that the same experimental procedure that produced the ΔH_f° for CH_3CHS was also utilized for the enthalpy of formation for H_2CS in the early 1980s (*61*) and was later found to underestimate the enthalpy of H_2CS by 28.1 kJ/mol (*62*). Under this assumption, we suspect that the experimental value for the ΔH_f° of CH_3CHS also should be re-examined.

3.2. *Bond dissociation enthalpies*

One of the few energetic properties that ccCA has not been extensively benchmarked against is BDE. A previous study on BDEs in sulfur compounds by Maung (*9*) has shown that a variety of methods including DFT, MP2, and CBS-*n* methods can produce results, which in some cases have errors as large as 41 kJ/mol, and none of the DFT, MP2, or CBS-*n* methods consistently produced the lowest error for every molecule with respect to experimental values. As shown in Table 3, the nine smaller alkylthiols and dialkylthiols from Maung's test set were evaluated with

Table 3. BDEs for various alkylthiol and diakylthiol chains determined using BDE $= \Delta H_f^\circ(A) + \Delta H_f^\circ(B) - \Delta H_f^\circ(A - B)$ and deviation from experiment Δ(BDE) reported in kJ/mol.

	BDEs							Δ(BDE)				
	ccCA-P	ccCA-S4	G3	G3B3	CBS-4[†]	Expt.[‡]	Uncert.[§]	ccCA-P	ccCA-S4	G3	G3B3	CBS-4[†]
HS-H	384.8	384.9	377.9	378.0	381.6	381.3	1.1	3.5	3.6	−3.4	−3.3	0.3
S-H	349.8	352.3	354.1	353.9	350.6	352.3	0.8	−2.5	0.0	1.8	1.6	−1.7
MeS-H	365.9	365.9	360.7	359.9	361.1	365.4	1.9	0.5	0.5	−4.7	−5.5	−4.3
Me-SH	315.0	315.1	304.5	305.2	315.1	312.7	1.4	2.3	2.4	−8.2	−7.5	2.4
Me-S	301.4	301.5	297.9	299.2	304.6	299.6	2.1	1.8	1.9	−1.7	−0.4	5.0
MeS-Me	309.5	309.5	300.6	300.3	307.9	309.1	2.9	0.4	0.4	−8.5	−8.8	−1.2
Et-SH	312.9	313.0	305.7	305.3	318.8	309.7	2.0	3.1	3.2	−4.1	−4.5	4.8
iPr-SH	313.1	313.1	308.8	307.6	361.1	365.4	1.9	3.4	3.4	−0.9	−2.1	9.1
tBu-SH	311.3	311.3	309.4	308.1	307.9	309.1	2.9	8.3	8.3	6.4	5.1	11.2
MAD								2.6	2.6	4.4	4.3	4.4
Std. Dev.								2.5	2.5	4.7	4.4	5.1
Thermo. Uncert.[¶]							1.8[‖]	7.0	7.1	10.3	10.1	11.3
Max. Dev.								8.3	8.3	8.5	8.8	11.2

[†]CBS-4 values from reference (9).
[‡]All experimental values are found in derived from experimental values listed in Table 1 and additional values for alkyl chains can be found in Section 3.2 within this manuscript.
[§]Thermochemical uncertainty corresponding to 95% confidence interval from experimental source.
[¶]Thermochemical uncertainty defined as the 95% confidence interval for the benchmarked methods estimated by twice the root mean square.
[‖]Average of the reported experimental uncertainty.

the ccCA, G3, and G3B3 methods. In the current study, the experimental BDEs were recalculated utilizing the enthalpy of formation data from Table 1 with experimental values of 147 ± 1 kJ/mol for CH_3 (*58*) and 120.9 ± 1.7, 90.0 ± 1.7, and 51.5 ± 1.7 kJ/mol for CH_3CH_2, $(CH_3)_2CH$, and $(CH_3)_3C$, respectively (*63*). This decision to recalculate the values for BDEs was made due to the large discrepancies between the values reported in Maung's work and the experimental enthalpies of formation listed in Table 1. To illustrate the impact of recalculating the BDEs, the MAD for Maung's CBS-4 results has been greatly decreased when utilizing these recalculated experimental values (4.4 versus 14.0 kJ/mol). For the BDEs, ccCA-P and ccCA-S4 produce excellent results with MADs of 2.6 kJ/mol from experimental values and 95% confidence intervals of ± 7.0 and ± 7.1 kJ/mol, respectively. In all the cases, the ccCA methodology overestimates the BDEs, varying by just over 0.0–8.3 kJ/mol. G3 and G3B3 produce results which show MADs of 4.4 and 4.3 kJ/mol, respectively, and 95% confidence intervals of ± 10.3 and ± 10.1. The MADs for BDE of the G*n* methods are reduced for this test set when compared with ΔH_f° s.

3.3. *Relative stabilities of selected isomers*

The relative energies for three sets of isomers are shown in Table 4, determined using ccCA-P, ccCA-S4, G3, and G3B3. Prior theoretical results have not been in agreement. For the SNO/NSO isomers, a study by Goumri *et al.* (*7*) shows NSO to be the most stable of the two isomers, as determined by the CBS-QB3 method. This is in disagreement with previous DFT calculations utilizing the functionals B3LYP, B3P86, and B3PW91 by Sun *et al.* (*64*), which indicated that the SNO isomer is the lowest in energy. CBS-QB3 is a model chemistry which approximates CCSD(T) results at the CBS limit and can be considered more rigorous and more reliable for relative energies than DFT and, thus, it is more likely that NSO is the lower of the two isomers (*7*). In the absence of experimental data, CBS-QB3 results have been simply used as a means of comparison with the current results. Although CBS-QB3 predicted NSO to be lower in energy by 8.0 kJ/mol than SNO, ccCA-P and ccCA-S4 predict 4.8 and 5.7 kJ/mol, respectively. G3, on the other hand, predicts a 20.8 kJ/mol difference in energy much higher than both CBS-QB3 and ccCA. Clearly, both of the ccCA formalisms and G3 agree with the CBS-QB3 results at least in sign, but remarkably G3B3 does not agree. G3B3 shows that SNO is lower in energy than NSO by 7.4 kJ/mol. This is interesting, considering that the only change from G3 to G3B3 is the use of B3LYP geometries and frequencies which both ccCA and CBS-QB3 utilize as well. This implies that the basis set utilized for the geometry optimization step can be critical, as ccCA, CBS-QB3, and G3B3 use B3LYP/cc-pVTZ, B3LYP/CBSB7, and B3LYP/6-31G(d) calculations for geometry optimizations, respectively.

Table 4.   Relative energy separation (with respect to the first listed molecule) of the NSO/SNO, SSF_2/FSSF, and HSO/SOH isomers reported in kJ/mol.

	ccCA-P	ccCA-S4	G3	G3B3	Expt./Theor.
ΔE_0 (NSO-SNO)	4.8	5.7	20.8	−7.4	
$\Delta_{iso}H_{298}$ (NSO-SNO)	4.4	5.3	20.5	−7.9	8.0[†]
ΔE_0 (SSF_2-FSSF)	6.1	6.4	5.7	6.6	
$\Delta_{iso}H_{298}$ (SSF2-FSSF)	7.0	7.2	6.8[‡]	7.4	11.3 ± 1.7[§]
ΔE_0 (HSO-SOH)	14.2	14.5	18.4	14.1	17.6[¶]
$\Delta_{iso}H_{298}$ (HSO-SOH)	14.2	14.5	18.3	14.2	

[†]CBS-QB3 results from reference (*7*).
[‡]From reference (*70*).
[§]Experimental result from reference (*65*)
[¶]CCSD(T) at the CBS limit results from reference (*19*).

The second set of isomers is FSSF and SSF_2, which have been studied experimentally by Lösking *et al.* (*65*) using photoionization mass spectrometry and by Cao *et al.* (*66*) using HeI photoelectron spectroscopy. In the case of Lösking *et al.* (*65*), they predict that SSF_2 is lower in energy by 11.3 ± 1.7 kJ/mol. Contrary to the work of Lösking, the study by Cao *et al.* (*66*) found that FSSF is the lower of the two isomers in part because previous theoretical work had shown FSSF to be the lower isomer. However, previous theoretical studies produce mixed results such as the extensive study done by Jursic (*67*) which showed that RHF, B3LYP, B3P86, BLYP, and BP86 all predict incorrectly that FSSF is the lower isomer, while the only density functional which correctly predicted the lower of the two isomers was SVWN. In a study by Prascher and Wilson (*68*), CCSD(T)/aug-cc-pVTZ calculation predicted SSF_2 to be the lower isomer at 0 K. Upon correction to 298 K, however, FSSF was shown to be lower in energy by 0.2 kJ/mol at this level of theory. CCSD(T)/CBS calculations have also been done by Ornellas (*69*), which included corrections for spin-orbit coupling, relativistic effects, and core-valence correlation. These CCSD(T)/CBS calculations are in agreement with the experimental work by Lösking (*69*) who predicted the $\Delta_{iso}H_{298}$ to be 8.8 kJ/mol, favoring SSF_2. MP2 calculations with B3P86 geometries correctly predicted that SSF_2 was the lower of the two isomers, which is an indication that the MP2-based ccCA should accurately predict the isomerization energy, as shown in Table 4. In a previous study by Ball (*70*), G2, G3, and CBS-QB3 were shown to correctly predict that SSF_2 was the lower of the two isomers. All four methods, ccCA-P, ccCA-S4, and G3B3 predict the isomerization energy to be within 4 kJ/mol of the experimental value.

The last set of isomers is the pair of molecules HSO and HOS which have previously been studied using MRCI, DFT, G2, and CCSD(T) (*11, 12, 19, 20, 71–78*). Experimental work has predicted that HSO is the lower of the two isomers (*79, 80*). Interestingly, it was not until 1993 that the HSO radical was shown to be more stable via computational methods (*11, 12*). All prior theoretical studies predicted HOS to be the more stable species. In 1993, Xantheas and Dunning (*11, 12*) showed via multireference *ab initio* calculations (CASSCF and CASSCF+1+2) utilizing the correlation-consistent basis sets that basis set choice has a substantial impact upon the correct identification of the lower energy isomer. In fact, when cc-pVDZ or cc-pVTZ basis sets were used, the incorrect isomer, HOS, was determined to be more stable. This can be attributed to the extraordinarily slow convergence of the energies of these species with respect to increasing basis set size. Once a basis set of at least quadruple-zeta quality (cc-pVQZ) is used, then the correct prediction is made. As the studies prior to 1993 utilized small basis sets, it is not surprising that they resulted in the incorrect prediction of the lower energy isomer. Since this time, there have been a number of studies, particularly those utilizing the tight *d* basis sets, which have correctly predicted the HSO isomer to be lower in energy, utilizing methods such as HF, CCSD, CCSD(T), G2, and B3LYP, provided that a large enough basis set is used (*19, 20, 75–78*).

As is shown in Table 4, all four methods correctly predict that HSO is lower in energy than SOH. Although no experimental data exist which try to quantify the energy difference, the CCSD(T) data at the CBS limit predict 17.6 kJ/mol (*20*). This is within good agreement with all four methods, although ccCA-P and ccCA-S4 underestimate this value by 3.4 and 3.1 kJ/mol, respectively.

4. Conclusion

Composite methods are invaluable in aiding experimentalists in numerous fields of chemistry. For sulfur-containing molecules, ccCA has been shown to be accurate. As compared with the G3 and G3B3 composite methods, ccCA has an improved accuracy and reliability for the systems studied as it produces a smaller MAD and does so without reliance upon an empirical fitting parameter. For enthalpies of formation, ccCA has an MAD of only 3.6 kJ/mol for the sulfur species studied, with a 95% confidence interval of ± 10.3 kJ/mol. For BDEs, the MAD for ccCA is larger, 2.6 kJ/mol,

and with a 95% confidence interval of 7.0 kJ/mol. For BDEs, the ccCA method is still more accurate than G3 and G3B3 for BDEs with an MAD of 1.8 and 1.7 kJ/mol lower than the MAD for both G*n* methods and shows a lower maximum deviation as compared with previous theoretical results (8.3 kJ/mol for ccCA-P and ccCA-S4 versus 11.2 and 8.5 for CBS-4 and G3, respectively). For isomerization energies, the ccCA method also correctly predicts the lowest isomers for three cases, SNO/NSO, FSSF/SSF$_2$, and HSO/SOH. The G3B3 method does not correctly predict that NSO has a lower energy than SNO, although the G3 method does. ccCA provides agreement to within 4.0 kJ/mol for energy of isomerization when compared with earlier work. Overall, the ccCA method does exceptionally well for energetic properties for sulfur-containing species due, in part, to the use of the cc-pV$(n + d)$Z basis sets, which composite methods such as G*n* do not utilize.

Acknowledgements

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