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A survey of factors contributing to accurate theoretical predictions of atomization energies and molecular structures

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High level electronic structure predictions of thermochemical properties and molecular structure are capable of accuracy rivaling the very best experimental measurements as a result of rapid advances in hardware, software, and methodology. Despite the progress, real world limitations require practical approaches designed for handling general chemical systems that rely on composite strategies in which a single, intractable calculation is replaced by a series of smaller calculations. As typically implemented, these approaches produce a final, or “best,” estimate that is constructed from one major component, fine-tuned by multiple corrections that are assumed to be additive. Though individually much smaller than the original, unmanageable computational problem, these corrections are nonetheless extremely costly. This study presents a survey of the widely varying magnitude of the most important components contributing to the atomization energies and structures of 106 small molecules. It combines large Gaussian basis sets and coupled cluster theory up to quadruple excitations for all systems. In selected cases, the effects of quintuple excitations and/or full configuration interaction were also considered. The availability of reliable experimental data for most of the molecules permits an expanded statistical analysis of the accuracy of the approach. In cases where reliable experimental information is currently unavailable, the present results are expected to provide some of the most accurate benchmark values available. © 2008 American Institute of Physics. [DOI: 10.1063/1.3008061]

I. INTRODUCTION

In two recent studies,^{1,2} we probed the limitations of a composite computational approach based primarily on coupled cluster theory and applied it to the difficult problem of predicting molecular atomization energies (heats of formation) to an accuracy of ± 1 kcal/mol or better, i.e., “chemical accuracy.” In addition, we examined the performance of the approach for determining molecular structures. Although single reference-based coupled cluster theory is clearly inappropriate for strongly multiconfigurational systems, such as the ²D excited state of the nitrogen atom or the NO₃ radical, it nevertheless has proven to be both remarkably powerful at recovering a large fraction of the correlation energy and broadly applicable to a wide range of chemical systems. The most commonly used single reference coupled cluster method, known as CCSD(T),³ involves single and double excitations, combined with a noniterative, quasiperturbative estimate of the effect of triple excitations. This method has been shown to be capable of treating systems with moderate multiconfigurational character, such as C₂ (¹Σ_g⁺) and O₃ (¹A₁),^{2,4} although additional corrections were required for these two molecules in order to achieve ± 1 kcal/mol with respect to experiment in the atomization energy. Consequently, the method has seen wide scale appli-

cation on a large number of molecules over the years.^{5–11} Despite a computational cost that grows as $\sim n^2 N^4 N_{it}$ for CCSD [with a single $n^3 N^4$ step for (T)], where n is the number of occupied orbitals, N is the number of unoccupied orbitals, and N_{it} is the number of CCSD iterations, with modern computer hardware it is possible to treat systems on the order of octane, C₈H₁₈, with quadruple ζ quality basis sets.¹² While extrapolation of the CCSD(T) energy to the complete basis set (CBS) limit has been discussed with basis sets of no more than triple ζ quality,^{13,14} it is our experience that such sets are inadequate for providing uniform accuracy for a wide variety of chemical species.

While our previous studies presented detailed breakdowns of the basis set convergence of individual contributions to atomization energies for a limited collection of five small molecules,^{1,2} results for a larger group of 68 molecules were restricted to a summary statistical analysis.² Karton *et al.* reported similar findings in separate studies of 30 small molecules¹⁵ and, more recently, of 9 diatomic molecules and water.¹⁶ Likewise, Harding *et al.*¹⁷ examined 26 small molecules in a comparable investigation. Our work relies upon data contained in the Computational Results Database (CRDB).¹⁸ The latest version of the CRDB holds $\sim 98\,000$ theoretical and experimental entries covering 321 molecular species and 42 atoms. We expand on our earlier work by surveying the individual component contributions to atomization energies for a much larger collection of 107 small molecules, selected from the complete list of molecules in the CRDB on the basis of the availability of higher order

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(HO) calculations. In addition, molecular structures obtained by the same computational procedure will be reported.

In common with other groups (see next section), it is our intent to document the strengths and weaknesses of advanced theoretical/computational methods for use in the prediction of a variety of chemical and physical properties. In many cases, corresponding experimental values are available for comparison. In other cases, the theoretical values provide a convenient benchmark for experiment or lower level calculations.

II. COMPUTATIONAL APPROACH

Our current composite approach represents the evolution of a strategy developed by us over the past decade in collaboration with other co-workers.^{4–10,19} As advances in computer hardware and software enabled ever more sophisticated theoretical techniques to be applied to small molecules, they were incorporated into our approach in order to improve the accuracy of the predicted energetics. Examples include coupled cluster theory with iterative triple excitations, as well as iterative and noniterative quadruple excitations.^{1,2,8,11,20–22}

Although our approach shares some of the basic steps of other coupled cluster-based methods in the literature, it also displays some differences. Many of the methods in the literature are defined as “model chemistries” and consist of a fixed recipe for the calculation of molecular geometries and energies. Examples include G1,²³ G2,²⁴ G3,²⁵ and G4,²⁶ as well as a large number of variants.²⁷ Other families of model chemistries include W_n [W1, W2,²⁸ W3,²⁹ W4, W4.2, W4.3,¹⁵ W4.4 (Ref. 16)], and HEAT_{xyz} [HEAT,³⁰ HEAT345-(Q), HEAT345-Q, HEAT345-Q(P), HEAT345-QP,³¹ HEAT-456QP (Ref. 17)]. Petersson and co-workers developed CBS model chemistries.³² Finally, Cundari and co-workers developed a variety of correlation consistent composite approaches, e.g., ccCA-aTV, ccCA-CBS-1, ccCA-CBS-2, ccCA-P, ccCA-S4, and ccCA-tm.³³ A number of these approaches include empirical parameters to adjust the electronic energies, with the goal of improving agreement with a collection of experimental data.

The driving force behind the proliferation of model chemistries is the desire to simultaneously address larger and more diverse systems, implying a reduction in the computational cost for a fixed system, while striving for higher accuracy, which normally requires greater computational cost. A model chemistry label, e.g., “G4,” is a convenient shorthand for an often complicated sequence of steps. Each step ideally contributes a roughly equivalent amount to the uncertainty in the final result, although in practice this is often not the case. When the G1 and G2 model chemistries were introduced, they were widely adopted because they provided a fast and relatively accurate approach to thermochemical calculations that was easily initiated via a single keyword in popular applications, such as the GAUSSIAN 9X and 03 codes.^{34,35} The first of the GX series of methods made use of well-founded, theoretically based corrections to the electronic energy. There is continued interest in improved approaches to the prediction of thermochemical properties associated with

minima and transition states on the potential energy surface. Progress in this area is facilitated by the introduction of new methods, advances in our understanding of the sources of error, and rapid increases in computer power. Although the number of model chemistries described in the chemical literature is already quite large, it is likely that the number will continue to grow as our understanding of electronic structure improves.

Unlike most of the approaches discussed in the previous paragraphs, the strategy we have developed lacks a simple name/abbreviation. Our current approach does *not* consist of a fixed recipe of steps involving predetermined basis set/method combinations. Instead, within an overall framework that combines coupled cluster theory and configuration interaction (CI) techniques with correlation consistent Gaussian basis sets,^{36–40} our approach permits a degree of flexibility that allows it to be fine-tuned for the varying accuracy requirements and individual natures of the chemical systems under study. The approach provides the freedom to avoid computing contributions that fall below the threshold of what is considered significant for a given target accuracy. It also allows us to easily incorporate information from the chemical literature when such information improves our results. As the focus is on predicting the heat of formation reliably, we can use the calculated heats of formation to predict chemical reaction energies and to build thermodynamic databases with practical estimates of the associated accuracies.

For small molecules, such as the ones considered in this work, our target accuracy for atomization energies (heats of formation) is generally on the order of 0.2–0.4 kcal/mol, i.e., much tighter than the chemical accuracy. In practice, the observed accuracy for a given collection of molecules can be better than that. For example, we reported² a mean absolute deviation (MAD) (ϵ_{MAD}) of 0.1 kcal/mol for a set of 19 small molecules with well-established experimental values taken from the Active Thermochemical Tables (ATCT), as given by Karton *et al.*¹⁵ The “focal point” technique of Allen and co-workers is another procedure that can best be regarded as a flexible strategy rather than a model chemistry.⁴¹ Flexible strategies such as ours can, of course, yield results of the same accuracy as model chemistries, such as HEAT and W4.*x*. In fact, for the 18 molecules in the latest HEAT paper¹⁷ and the 30 molecules in the latest W4 papers^{15,16} that overlap this work, all atomization energies agree to within ~0.2 kcal/mol except for one W4 value (that for ClCN which differs by 0.4 kcal/mol). While this paper was nearing completion, we became aware of a larger (99 molecule) compilation of W4, W4.2, W4.3, and W4.4 atomization energies.⁴²

In general terms, our current approach relies on (1) the ability to exploit the systematic one-particle basis set convergence of correlation consistent basis sets, (2) the rapid decrease in basis set requirements as the excitation level in the *n*-particle expansion is increased, and (3) the ability to decomposed the problem into additive pieces. Items (1) and (2) will be discussed in greater detail in subsequent sections. The assumption entailed in item (3) can only be partially tested since the computational expense of extended basis set, all-electron, relativistic, full configuration interaction (FCI) cal-

culations even on diatomic molecules currently places them out of reach. Limited tests of the additivity assumption for frozen core (FC), core/valence (CV), and scalar relativistic (SR) components on first row diatomic molecules indicates that the assumption introduces an uncertainty on the order of 0.0001 Å for bond lengths and 0.01–0.03 kcal/mol for electronic dissociation energies (D_e for diatomics and ΣD_e for polyatomics), both of which are of minor importance. As part of this study, a further test was performed on Br₂, where the relativistic effects might be less separable. Combining CV and SR corrections in a single calculation (with an appropriately modified basis set) produced negligible differences with respect to results predicted by adding separate CV and SR corrections in FC CCSD(T) calculations. However, care must be taken in cases where there are large changes in the oxidation state between the atom in the molecule relative to the isolated atom.⁴³ There are also potential issues with the use of effective core potentials and the need to include additional functions to describe the inner shell electrons, as will be discussed in a subsequent section.⁴⁴

The HEAT model chemistry³⁰ does not decompose the CCSD(T) correlation energy into FC and CV pieces. In the most recent HEAT paper,¹⁷ the authors emphasized the potential for error resulting from the FC and CV additivity approximations: "...those working in this area *must* begin to entertain the idea of abandoning separate treatments of core and valence correlation..." To test this conclusion, we conducted a further test of the FC/CV additivity approximation on the hydrogen peroxide molecule, H₂O₂, by carrying out a series of all-electron correlated calculations with the aug-cc-pwCVnZ, $n=T, Q,$ and 5, basis sets. For the sake of this test, geometry optimization was judged to be unimportant. All calculations were performed at the optimal cc-pwCV5Z geometry. This yielded a vibrationless atomization energy of 268.69 ± 0.44 kcal/mol using the CBS extrapolation procedure described below. The combination of a FC aug-cc-pVnZ ($n=T, Q,$ and 5) CBS extrapolation with a CV cc-pwCVnZ ($n=T, Q,$ and 5) CBS correction yielded $\Sigma D_e = 268.59 \pm 0.44$ kcal/mol. The 0.10 kcal/mol error associated with the additivity approximation is small compared to the uncertainty in the CBS extrapolations. Furthermore, as will be seen, we often combine FC CBS estimates obtained with an aug-cc-pVnZ basis set with CV CBS corrections obtained with cc-pwCV($n-1$)Z basis sets. In the case of H₂O₂, this implies combining an aug-cc-pV6Z FC basis set calculation with the cc-pwCV5Z CV set result. Such a combination yields $\Sigma D_e = 268.70 \pm 0.20$ kcal/mol. Not only is this value in close agreement with the aug-cc-pwCVnZ extrapolation, but the error bars have been considerably reduced. We decompose the correlation problem into FC and CV parts because of the computational savings to be obtained by exploiting the different convergence rates of the two parts. The FC contribution to the atomization energy converges more slowly with respect to the one-particle expansion than the CV contribution, unlike the magnitude of the CV correlation energy.⁴⁵ Thus, it requires a higher level basis set to reach the same degree of convergence.

A. General computational considerations

All CCSD(T) calculations were performed with MOLPRO 2006.1.⁴⁶ Open shell calculations were based on the R/UCCSD(T) method, which begins with restricted open shell Hartree–Fock (ROHF) orbitals but allows a small amount of spin contamination in the solution of the CCSD equations. It is requested in MOLPRO with the keyword "UCCSD(T)." Full atomic symmetry on the orbitals was imposed when evaluating atomic CCSD(T) energies. Atomic symmetry was not imposed in CCSDT, CCSDTQ,⁴⁷ and FCI calculations. At the FCI(FC)/cc-pVDZ level, imposing atomic symmetry raises the C (³P) energy by only 2.3 μE_h . Of course, when all electrons are correlated the FCI energy becomes invariant to the choice of orbitals.

Unless otherwise noted, CCSD(T) geometries were optimized at every basis set level to the default convergence criterion in MOLPRO, i.e., the maximum component of the gradient is less than 3×10^{-3} a.u. and the maximum energy change is less than 1 μE_h . Spectroscopic properties (r_e , D_e , and ω_e , among others) for diatomic molecules were obtained from a sixth degree Dunham fit of the potential energy curve.⁴⁸ There were two exceptions to the use of optimized structures in this study. The first occurred with the largest polyatomic molecules at the CCSDTQ level of theory, where an individual energy evaluation might take three days or more. The second is associated with CCSDTQ calculations performed with the cc-pwCVnZ basis sets. In both cases, the CCSDTQ energies were evaluated at the optimal CCSD(T) geometries. CCSDT, CCSDTQ, and CCSDTQ5 calculations were performed with the MRCC program of Kállay and Surján⁴⁹ interfaced to MOLPRO.

B. Frozen core CCSD(T)

All CCSD(T)(FC) energies, geometries, and harmonic frequencies were obtained with the correlation consistent basis set family. In particular, the CBS limit for first row elements was estimated with the diffuse function augmented sequence of basis sets, aug-cc-pVnZ, $n=D, T, Q, 5, 6,$ and 7, for first row elements.^{19,36,50} The most extensive of these, denoted aug-cc-pV7Z, contains multiple shells of k functions ($\ell=7$). Explicit inclusion of k functions was only possible in a few cases. In the rest of the cases, the k function contribution was estimated by exploiting the uniformity in the correlation energy convergence pattern as a function of ℓ , as described elsewhere.^{1,19,22} For second row elements, the aug-cc-pV($n+d$)Z basis sets were chosen in order to address the well-known need for tight d functions.⁵¹ Some bromine-containing molecules were treated with a newly developed aug-cc-pV6Z basis set. Among the molecules examined in this study, it was possible to treat almost 90% of them with sextuple zeta quality basis sets or better. The largest CCSD(T)(FC)/aug-cc-pV6Z calculation used in this study was performed on ethane and involved 1140 basis functions.

The current iodine basis sets and relativistic, small-core pseudopotential were taken from the most recent work of Peterson *et al.*⁵² These are denoted aug-cc-pVnZ-PP, $n=D, T, Q,$ and 5. Preliminary versions of the sets were previously used in a study of the heats of formation of small haloge-

nated compounds, including HI ($1\Sigma^+$) and I₂ ($1\Sigma_g^+$).⁹ Peterson *et al.*⁵³ also reported results for HI in subsequent development work on a second generation of basis sets and pseudopotentials for elements from groups 16–18. An extensive study of the use of these basis sets for the iodofluorides showed that significant care was needed in handling tight functions.⁴⁴

Although our calculations utilized some of the largest Gaussian basis sets available in the chemical literature, the magnitude of the residual basis set truncation error easily exceeds the tolerance required for high accuracy thermochemical work. A brute force approach to reducing the error is impractical if we limit ourselves to conventional methods since they scale very steeply in terms of computational cost. Alternative approaches, such as the explicitly correlated R12 methods of Klopper and co-workers,⁵⁴ address this issue but still require large basis sets for high accuracy. The recently developed F12 methods may ultimately prove more efficient, but these have yet to be incorporated into existing thermochemical methodologies.⁵⁵

In order to minimize the basis set truncation error while simultaneously keeping the one-particle expansion within practical limits, we exploited the systematic convergence of the correlation consistent basis sets through the use of CBS extrapolation formulas. From among the many such formulas in the literature, we have selected five in deriving our best estimate. These include an exponential,⁵⁶ a mixed Gaussian/exponential,⁵⁷ two inverse powers of ℓ_{\max} , where ℓ_{\max} is the highest angular momentum present in the basis set⁵⁸ and an expression suggested by Schwenke.¹⁴ The choice of which extrapolation methods to use is not unique. It is based on our experience in applying a variety of extrapolation formulas to many chemical species. The rationale for this choice has been discussed previously.¹ With the first four formulas, we have chosen to extrapolate the total energy rather than to perform separate extrapolations on the self-consistent field (SCF), CCSD, and (T) correlation components, as has been our practice for many years. For basis sets of the quality used in this study, the change in the correlation component far exceeds any change associated with the SCF component. In the past, the *Wn* and HEAT models have included separate SCF extrapolations. However, in the most recent HEAT paper¹⁷ the following was noted: “In fact, it seems that there is little point in doing extrapolations of the HF-SCF energy at all.” Jensen⁵⁹ and Karton and Martin⁶⁰ recently discussed approaches to estimating the Hartree–Fock (HF) limit.

In previous work, we found that no single formula clearly outperforms all others for every chemical system and combination of basis sets.^{1,9,22} Consequently, the average of the five formulas serves as our best estimate of the CBS limit and the spread among the estimates can be interpreted as a crude gauge of the uncertainty in the extrapolations. Although there are no formal reasons for choosing this average, in practice it appears to produce reasonable results. Frequently, the average is more stable than any individual formula and the relatively conservative error bars usually encompass, or nearly encompass, the next larger basis set estimate, as shown in Fig. 1 for C₂ and CO₂. The exponential

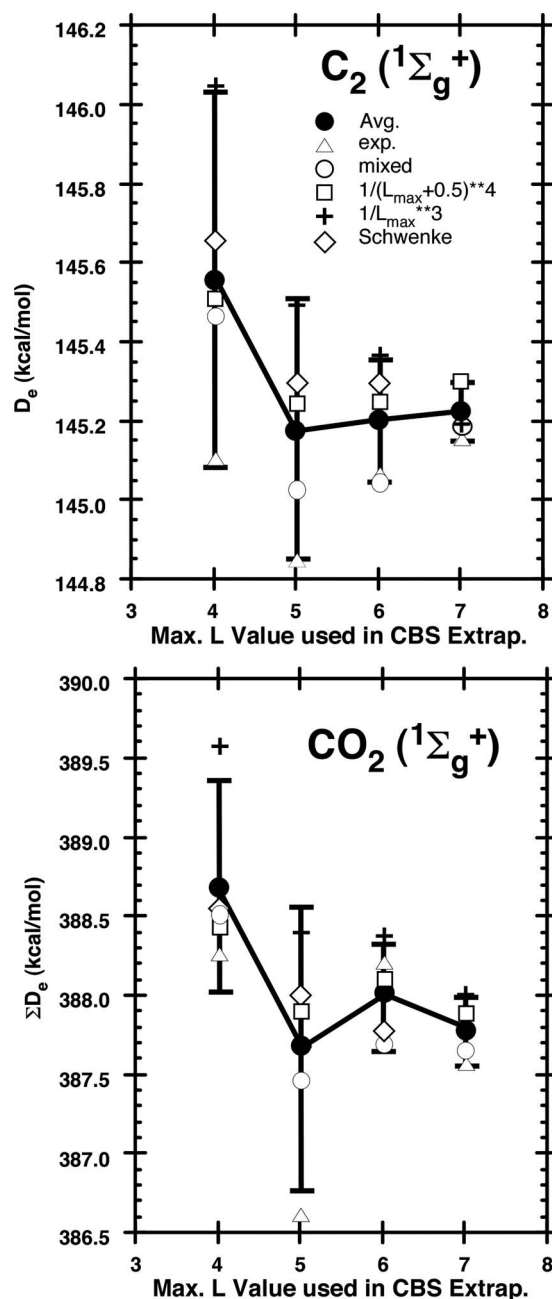


FIG. 1. Variation in the frozen core CCSD(T) CBS estimates as function of the underlying basis sets for C₂ and CO₂. The error bars are taken to be \pm half the spread in the values.

function often underestimates the CBS limit, whereas the $1/\ell_{\max}^3$ formula tends to overestimate it. The latter observation was corroborated in the latest HEAT paper.¹⁷ In other works, Peterson and co-workers^{61,62} and Denis⁶³ found the average of the mixed and $1/\ell_{\max}^3$ formulas to work well. Despite the use of large basis sets and extrapolation formulas to minimize the residual basis set truncation error, we nonetheless find the uncertainty in estimating the CCSD(T)(FC) CBS limit to be a leading source of uncertainty in the final or “best” values reported.

In analogy to the situation with atomization energies, some correction for the basis set truncation error is also required for high level molecular structure determinations. The two cases differ only in the magnitude of the effect, with the

corrections for bond lengths and bond angles generally being smaller. With basis sets of quintuple or sextuple ζ quality, bond and dihedral angles are typically converged to 0.03° or better. Bond lengths can still deviate from the apparent CBS limit by $0.002\text{--}0.004 \text{ \AA}$ depending on the system. Although experimental bond lengths in diatomic molecules can often be measured with an accuracy of 0.0001 \AA or better, for polyatomic species it is rare to find r_e values of the same quality. The typical “bottom of the well” values obtained from electronic structure methods are not directly comparable to the assortment of values (r_0 , r_g , r_a , r_z , etc.) obtained from spectroscopic or diffraction-based experimental measurements.⁶⁴ Recent advances that combine experimental and theoretical information, leading to “semiexperimental” structures, show much promise.⁶⁵ Although the number of comparisons is limited, the level of agreement between semiexperimental structures and coupled cluster theory structures has been found to be excellent.^{66,67} The semiexperimental results used in the present study are taken from the work of Craig *et al.*⁶⁸ and Gauss *et al.*⁶⁹ With these considerations in mind, our target accuracies for polyatomic structures are $\pm 0.001 \text{ \AA}$ and $\pm 0.2^\circ$. An earlier study reported $\varepsilon_{\text{MAD}} = 0.0014 \text{ \AA}$ (AH bonds, 34 comparisons) and 0.0007 \AA (AB bonds, 51 comparisons).²

The most straightforward way to estimate CBS structural parameters is to apply one or more of the extrapolation formulas directly to the molecular energies, followed by a surface fit. For diatomics this is a simple matter, but for polyatomics such a grid is typically unavailable and would represent a significant, additional computational expense. Another alternative is to compute derivatives with respect to the CBS energies, as suggested by Heckert *et al.*⁷⁰ and recently used by Puzzarini *et al.*⁷¹ Finally, we have found through experience that a simple exponential fit of the optimized bond lengths obtained from a sequence of correlation consistent basis sets works quite well, at least for molecules composed of first and second row elements. Figure 2 shows the approximately exponential decay of the N_2 CCSD(T)(FC) ground state bond lengths as a function of the basis set. Similar information is provided in Table I for the diatomics N_2 , S_2 , and Br_2 . Several trends are evident. First, the size of the basis set truncation error for a fixed basis set level increases as one progresses down the Periodic Table. The aug-cc-pVTZ error for Br_2 is more than four times the error for N_2 . The exponential extrapolation cuts the error in half or more for N_2 and S_2 but yields erratic results for the heavier Br_2 . CBS bond lengths based on extrapolations of the total energy do not show the same erratic behavior for Br_2 . In the present work, we will adopt the practice of approximating CBS bond lengths in diatomics by extrapolating total energies with exponential and $1/\ell_{\text{max}}^3$ formulas and use half the difference in the two values as an estimate of the uncertainty. Unless otherwise noted, for polyatomics we will directly extrapolate the bond lengths.

The assignment of reasonable error bars to any atomic or molecular property predicted by electronic structure calculations is challenging. Unlike experimental measurements, electronic structure calculations are completely deterministic. Repeating a calculation multiple times on different com-

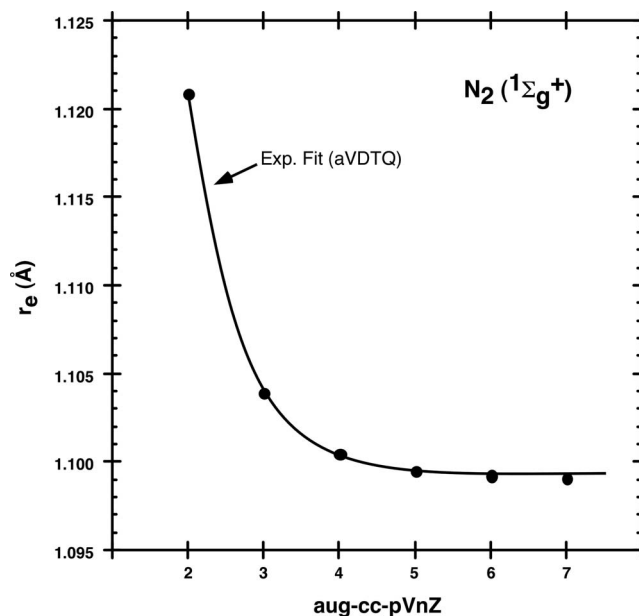


FIG. 2. Bond length convergence for N_2 as a function of basis set at the CCSD(T)(FC) level of theory.

puters with different applications should result in the same answer every time, within the convergence tolerances and numerical precision of each code. In the absence of practical formal tools for assigning uncertainty, most researchers have resorted to two fundamental alternatives.

The first is essentially a plausibility argument based on statistics and relies on a presumed accurate set of reference data, such as those provided by the ATcT (Ref. 72) for heats of formation. This argument runs as follows: if a computational protocol demonstrates the ability to reproduce the reference set values within a certain tolerance, it is reasonable to expect a similar level of accuracy for molecules outside the reference set. Obviously, the larger and more diverse the reference set is, the stronger the case can be made. This approach has been used with the Wn , HEAT, and ccCA model chemistries. A related issue is the choice of which statistical measure to use. In the past, theoreticians have often reported the MAD or the root mean square (rms) deviation, while experimentalists prefer to quote a 95% confidence interval, which corresponds to roughly two standard deviations.

A second approach, which we have promoted in earlier papers,^{1,2} relies on a molecule-by-molecule analysis of the major sources of error to the property of interest. Because it provides an estimate of the uncertainty that is specific for each molecule and is independent of a reference set, it avoids making the assumption that new chemical systems are “similar enough” to the reference set to expect a similar accuracy. Both approaches have their merits and each will be reported in this study. Of the two, the second is more stringent since a worst case scenario requires that all error be additive, whereas in reality many errors fortuitously cancel.

C. Core/valence and scalar relativistic CCSD(T)

For many molecules, after the FC property has been extrapolated to the CBS limit, the next most important correc-

TABLE I. CCSD(T)(FC) bond length convergence for N₂, S₂, and Br₂ in their ground states.

Basis set	r_e (Å)	Raw error ^a	CBS (expt.)	Extrap. error ^b
N ₂ (¹ Σ _g ⁺)				
aug-cc-pVDZ	1.1209	0.0220		
aug-cc-pVTZ	1.1040	0.0051		
aug-cc-pVQZ	1.1005	0.0016	1.0996	0.0007
aug-cc-pV5Z	1.0995	0.0006	1.0992	0.0003
aug-cc-pV6Z	1.0993	0.0004	1.0991	0.0002
aug-cc-pV7Z	1.0991	0.0002	1.0989	0.0000
Est. CBS(expt.) ^c	1.0989			
Est. CBS(1/ℓ _{max} ³) ^d	1.0988			
S ₂ (³ Σ _g ⁻)				
aug-cc-pV(D+d)Z	1.9249	0.0336		
aug-cc-pV(T+d)Z	1.9059	0.0146		
aug-cc-pV(Q+d)Z	1.8969	0.0056	1.8886	-0.0027
aug-cc-pV(5+d)Z	1.8939	0.0026	1.8924	0.0011
aug-cc-pV(6+d)Z	1.8926	0.0013	1.8917	0.0004
Est. CBS(expt.) ^c	1.8917			
Est. CBS(1/ℓ _{max} ³) ^d	1.8909			
Br ₂ (¹ Σ _g ⁺)				
aug-cc-pVDZ	2.3530	0.0619		
aug-cc-pVTZ	2.3127	0.0216		
aug-cc-pVQZ	2.2986	0.0075	2.2909	-0.0002
aug-cc-pV5Z	2.2946	0.0035	2.2929	0.0018
aug-cc-pV6Z	2.2921	0.0010	2.2882	-0.0029
aug-cc-pV7Z ^e	2.2916	0.0005	2.2915	0.0004
Est. CBS(expt.) ^c	2.2915			
Est. CBS(1/ℓ _{max} ³) ^d	2.2907			

^aError in the raw CCSD(T) bond lengths with respect to the average of the CBS(expt.) and CBS(1/ℓ_{max}³) estimates obtained by extrapolating the total energies and performing a Dunham fit.

^bError in the exponential extrapolation of the bond lengths.

^cCBS estimate obtained by performing an exponential extrapolation of the total energies.

^dCBS estimate obtained by performing a 1/ℓ_{max}³ extrapolation of the total energies.

^eOptimization performed without *k* functions.

tion to the property arises from correlating outer core electrons, i.e., the (1*s*²) core electrons for first row elements, the (2*s*²)(2*p*⁶) core for second row elements, etc. We denote this correction to the atomization energy as Δ*E*_{CV} and will sometimes refer to CV results as “all electron.” For the purpose of computing CV corrections to atomization energies and molecular structures, we chose the weighted CV basis sets, cc-pwCV*n*Z.³⁹ Some of the older corrections stored in the CRDB were performed with the original correlation consistent CV sets, cc-pCV*n*Z.^{38,73} The weighted basis sets are normally more rapidly convergent than the original sets. CV corrections were computed as the difference between the CCSD(T)(FC) and CCSD(T)(CV) properties using the same CV basis set and evaluated at their respective optimized geometries. CV corrections were also extrapolated to the CBS limit. If we again adopt the spread in CBS estimates among the five extrapolation formulas discussed earlier, the uncertainty arising from the CV extrapolation was an order of magnitude or more smaller than the FC counterpart. In the absence of published CV basis set parameters for the

Schwenke formula, the cc-pV*n*Z parameters were used instead. Despite the lack of CV-specific parameters, the Schwenke formulas yielded very similar results to the other formulas.

Next in terms of importance to the electronic component of the atomization energy is the SR correction, Δ*E*_{SR}. For molecules composed of first and second elements, this correction is generally smaller in magnitude than Δ*E*_{CV}, although exceptions are not difficult to find, e.g., H₂S (¹A₁). SR corrections were obtained from second order Douglas–Kroll–Hess CCSD(T)(FC) calculations⁷⁴ using the cc-pVTZ-DK, cc-pVQZ-DK and cc-pV5Z-DK basis sets.⁷⁵ The correction is seldom sensitive to the size of the basis set or level of theory. Although they will not be discussed in detail in the present work, the CRDB also contains results for first row transition metals,⁴⁰ as well as third and fourth row, main group compounds.^{53,76} The specification of the largest basis sets used for the various components, e.g., CCSD(T)(FC), CCSD(T)(CV), and CCSD(T)-DK, is given in Table II.

D. Spin-orbit corrections

The contribution of atomic spin-orbit (SO) coupling must be considered for high accuracy atomization energies. Our nonrelativistic atomic calculations describe an average multiplet state, requiring a shift in the energy of the atomic asymptotes which has the effect of decreasing the atomization energy. Although the atomic multiplet splittings could be obtained from theory, we have chosen to use the tabulated values of Moore.⁷⁷ Atomic SO corrections are relatively small for first row elements but can be substantial in heavier atoms. For example, the value in I is 7.24 kcal/mol. In some cases, e.g., NO (²II), molecular first order SO effects will also contribute to the atomization energy. These molecular values were either taken from experiment⁷⁸ or computed. Molecules composed of heavier elements (*Z* > 18) can also possess non-negligible, second order SO corrections.^{9,52,61} Previous second order corrections for molecules such as HI and I₂ relied on first order CI calculations with preliminary versions of the aug-cc-pVTZ-PP basis set and pseudopotential. In the case of HI, the calculation of the second order correction was repeated with the latest iodine basis sets and pseudopotentials and a full valence, complete active space (CAS) CI. The SO correction changed by only 0.02 kcal/mol, from -0.52 to -0.50 kcal/mol. For I₂, we used a recently published value from Shepler *et al.*⁷⁹

E. Higher order correlation

Contributions to atomization energies and structures from correlation recovery beyond CCSD(T) are normally lumped under the heading of “HO” effects. In the present context, such effects will be obtained from CCSDT, CCSDT(Q), and CCSDTQ coupled cluster methods. As resources permitted, CCSDTQ5 and FCI calculations were also used. The literature contains a slowly growing body of information on the impact of HO effects on the two properties of interest in this paper.^{1,2,8,15,16,21,22,29–31,80–82} In the present work, no attempt was made to extrapolate HO corrections to the CBS limit, as was done in several recent studies.^{16,29,30} While it

TABLE II. Basis set specification for individual components. The largest basis set used for each component is listed under the appropriate column. Open shell CCSD(T) were performed with the R/UCCSD(T) method. Atomic asymptotes were described by symmetry-equivalent orbitals. Basis set designations: aVQZ=aug-cc-pVQZ, aV5Z=aug-cc-pV5Z, aV6Z=aug-cc-pV6Z, aV7Z=aug-cc-pV7Z, aV(Q+d)Z=aug-cc-pV(Q+d)Z, aV(5+d)Z=aug-cc-pV(5+d)Z, aV(6+d)Z=aug-cc-pV(6+d)Z, aV(7+d)Z=aug-cc-pV(7+d)Z, aV5Z-PP=aug-cc-pV5Z-PP, CVTZ=cc-pCVTZ, CVQZ=cc-pCVQZ, CV5Z=cc-pCV5Z, CV6Z=cc-pCV6Z, wCVTZ=cc-pwCVTZ, wCVQZ=cc-pwCVQZ, wCV5Z=cc-pwCV5Z, VDZ_DK=cc-pVDZ_DK, VTZ_DK=cc-pVTZ_DK, VQZ_DK=cc-pVQZ_DK.

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
H ₂ (¹ Σ _g ⁺)	aV7Z	NA	NA	aV7Z	NA
LiH (¹ Σ _g ⁺)		CV5Z(Li)/ aV5Z(H)	VTZ_DK(Li)/ aVTZ_DK(H)	CV5Z	FCI(CV)/ CVTZ(Li)/ aVTZ(H)
Li ₂ (¹ Σ _g ⁺)		CV5Z(Li)	VTZ_DK(Li)	Expt.	NA
HCl (¹ Σ _g ⁺)	aV(6+d)Z(Cl)/ aV6(H)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
HBr (¹ Σ _g ⁺)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
HI (¹ Σ _g ⁺)	aV5Z-PP	wCVQZ	None	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
ClO (² Π)	aV(6+d)Z(Cl)/ aV6(O)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
HOCl (¹ A')	aV(6+d)Z(Cl)/ aV6(O)	wCV5Z	VTZ_DK	CBS ^c	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
BeH (² Σ _g ⁺)	aV6Z	CV5Z(Be)/ aV5Z(H)	VTZ_DK(Be)/ aVTZ_DK(H)	Expt.	FCI/VTZ
BH (¹ Σ _g ⁺)	aV6Z	wCV5Z	VTZ_DK	Expt.	FCI/aVQZ
B ₂ (³ Σ _g ⁻)	aV6Z	wCV5Z	VTZ_DK	Expt.	RCCSDT/VQZ+ FCI/VTZ+ HO CVQZ/CVTZ ^d
B ₂ H ₆ (¹ A _g)	aV5Z	wCVQZ	VTZ_DK	aVQZ/aVDZ	CCSDT/VTZ+ CCSDQ/VDZ+ cf est. FCI/VDZ
BN (³ Π)	aV6Z	wCV5Z	VTZ_DK	Expt.	RCCSDT/VQZ+ FCI/VTZ+ HO CVQZ/CVTZ ^d
BO (² Σ _g ⁺)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
BF (¹ Σ _g ⁺)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ CCSDTQ(CV)/wCVDZ
BP (³ Π)	aV(6+d)Z(P)/ aV6(B)	wCV5Z	VTZ_DK	aV(6+d)Z	RCCSDT/VQZ+ FCI/VTZ+ CCSDTQ(CV)/wCVDZ
BCl (¹ Σ _g ⁺)	aV(6+d)Z(Cl)/ aV6(B)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
CH (² Π)	aV6Z	aCV5Z	VTZ_DK	Expt.	FCI/VQZ+ CCSDTQ(CV)/wCVDZ
CH ₂ (³ B ₁)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ

TABLE II. (Continued.)

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
CH ₂ (¹ A ₁)	aV7Z	wCV5Z	VTZ_DK	aV5Z/ aVDZ	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
CH ₃ (¹ A ₂ '')	aV7Z	wCV5Z	VTZ_DK	Hybrid anh. ^c	CCSDT/VTZ+ CCSDTQ/VDZ+ FCI/VDZ
CH ₄ (¹ A ₁)	aV7Z	wCV5Z	VTZ_DK	Hybrid anh.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ CCSDTQ(CV)/wCVDZ
NH (³ Σ ⁻)	aV7Z	wCV5Z	VTZ_DK	Expt.	FCI/VQZ+ CCSDTQ(CV)/wCVTZ
NH ₂ (² B ₁)	aV6Z	wCV5Z	VTZ_DK	aVQZ/aVTZ	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
NH ₃ (¹ A ₁)	aV6Z	wCV5Z	VTZ_DK	VQZ ^f	CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VDZ
OH (² Π)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ FCI/VTZ
HF (¹ Σ ⁺)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/V5Z+ CCSDTQ/VQZ+ FCI/VDZ
C ₂ (¹ Σ _g ⁺)	aV7Z	CV6Z	V5Z_DK	Expt.	CCSDTQ/VQZ+ FCI/VTZ(diff.s,p)+ HO CVQZ/CVTZ ^d
C ₂ H (² Σ)	aV7Z	wCV5Z	V5Z_DK	VQZ	CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VTZ+ CCSDTQ(CV)/wCVDZ
C ₂ H ₂ (² Σ _g ⁺)	aV7Z	wCV5Z	VTZ_DK	VTZ	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ HO CVQZ/CVTZ ^d
C ₂ H ₄ (¹ A _g ')	aV6Z	wCV5Z	VTZ_DK	aVQZ/aVTZ	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
C ₂ H ₆ (¹ A _{1g})	aV6Z	wCVQZ	VTZ_DK	aVQZ/aVTZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
C ₃ H ₆ cyclopropane	aV5Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
C ₄ H ₆ butadiene	aV5Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	Scaled CCSDT(Q)+ cf est. FCI/VDZ
HOF (¹ A')	aV6Z	CV5Z	VQZ_DK	aVQZ/VTZ	CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VDZ
HCO (¹ A')	aV7Z	wCV5Z	VTZ_DK	aVQZ/aVTZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
H ₂ CO (A ₁)	aV7Z	wCV5Z	VTZ_DK	aVQZ/aVDZ	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ

TABLE II. (Continued.)

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
CO (¹ Σ^+)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ HO CVQZ/CVTZ ^d
CO ₂ (¹ Σ_g^+)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
CF (² Π)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ CCSDTQ(CV)/wCVDZ
CF ₂ (¹ A_1)	aV6Z	wCV5Z	VTZ_DK	aVQZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CF ₃ (² A_1)	aV6Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CN (² Σ^+)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ HO CVQZ/CVTZ ^d
C ₂ N ₂ (¹ Σ_g^+)	aV6Z	wCVQZ	VTZ_DK	aVTZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CS (¹ Σ^+)	aV(7+d)Z(S)/ aV7Z(C)	wCV5Z	V5Z_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VTZ+ CCSDTQ(CV)/wCVDZ
CS ₂ (¹ Σ_g^+)	aV(7+d)Z(S)/ aV7Z(C)	wCVQZ	VQZ_DK	aV(T+d)Z	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
OCS (¹ Σ^+)	aV(6+d)Z(S)/ aV6Z(C,O)	wCV5Z	VTZ_DK	aV(T+d)Z	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
NO (² Π)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ HO CVQZ/CVTZ ^d
HNO (¹ A')	aV7Z	wCV5Z	VTZ_DK	VQZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
N ₂ (¹ Σ_g^+)	aV7Z	wCV5Z	V5Z_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ FCI/VTZ+ HO CVQZ/CVTZ ^d
NF (³ Σ)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
NF ₂ (³ B_1)	aV6Z	CV5Z	VTZ_DK	aVQZ/VTZ	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
NF ₃ (¹ A_1)	aV5Z	CVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ

TABLE II. (Continued.)

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
NP ($^1\Sigma^+$)	aV(6+d)Z(P)/ aV6Z(N)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VDZ
N ₂ O ($^1\Sigma^+$)	aV7Z	wCV5Z	VTZ_DK	VQZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
NO ₂ (2A_1)	aV7Z	wCV5Z	VTZ_DK	VQZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
O ₂ ($^3\Sigma_g^-$)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ HO CVQZ/CVTZ ^d
O ₃ (1A_1)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ CCSDTQ(5)/VDZ+ cf est. FCI/VDZ+ CCSDT(Q)(CV)/wCVDZ
F ₂ ($^1\Sigma_g^+$)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ HO CVQZ/CVTZ ^d
F ₂ O (1A_1)	aV6Z	CV5Z	VTZ_DK	VQZ/VTZ ^e	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
H ₂ O (1A_1)	aV7Z	wCV5Z	VQZ_DK	Expt.	CCSDT/VQZ+ FCI/VTZ(O),VDZ(H)
H ₂ O ₂ (1A)	aV6Z	wCV5Z	VTZ_DK	VQZ	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
FO ($^2\Pi$)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VTZ+ CCSDTQ(CV)/wCVDZ
FOO ($^2A''$)	aV6Z	wCV5Z	VTZ_DK	aVTZ	CCSDT/VQZ+ CCSDTQ/VDZ+ CCSDTQ5/VDZ(no d)+ cf est. FCI/VTZ+ CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
PH ₃ (1A_1)	aV(6+d)Z(P)/ aV6Z(H)	wCV5Z	VTZ_DK	VQZ	CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
P ₂ ($^1\Sigma_g^+$)	aV(6+d)Z	wCV6Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
S ₂ ($^3\Sigma_g^-$)	aV(7+d)Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ

TABLE II. (Continued.)

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
SO (³ Σ ⁻)	aV(6+d)Z(S)/ aV6Z(O)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
SO ₂ (¹ A ₁)	aV(6+d)Z(S)/ aV6Z(O)	wCV5Z	VQZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
SO ₃ (¹ A ₁ ['])	aV(6+d)Z(S)/ aV6Z(O)	wCV5Z	VQZ_DK	aVQZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ
ClF (¹ Σ ⁺)	aV(6+d)Z(Cl)/ aV6Z(F)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
BrO (² Π)	aV6Z	wCV5Z	VTZ_DK	aV6Z	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
BrF (¹ Σ ⁺)	aV6Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
BrCl (¹ Σ ⁺)	aV6Z(Br)/ aV(6+d)Z(Cl)	wCV5Z	VTZ_DK	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
Cl ₂ (¹ Σ _g ⁺)	aV(7+d)Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
Br ₂ (¹ Σ _g ⁺)	aV6Z	wCV5Z	VQZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
SiO (¹ Σ ⁺)	aV(6+d)Z(Si)/ aV6Z(O)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ CCSDTQ(CV)/wCVDZ
HS (² Π)	aV(6+d)Z(S)/ aV6Z(H)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ+ CCSDTQ(CV)/wCVDZ
H ₂ S (¹ A ₁)	aV(6+d)Z(S)/ aV6Z(H)	wCV5Z	VTZ_DK	Expt.	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ
Si ₂ (³ Σ _g ⁻)	aV(6+d)Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VDZ
HO ₂ (² A ['])	aV7Z	CV6Z	V5Z_DK	VQZ	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
ClCN (¹ Σ ⁺)	aV(6+d)Z(Cl)/ aV6Z(C, N)	wCV5Z	VTZ_DK	VQZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
HONO (¹ A ['])	aV6Z	wCV5Z	VTZ_DK	VTZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+ CCSDT(Q)(CV)/wCVDZ
Al ₂ (³ Π _u)	aV(6+d)Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ FCI/VTZ

TABLE II. (Continued.)

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
PO (² Π)	aV(6+d)Z(P)/ aV6Z(O)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
FS (² Π)	aV(6+d)Z(S)/ aV6Z(F)	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
CF ₂ O (¹ A ₁)	aV6Z	CVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ
CH ₂ F ₂ (¹ A ₁)	aV6Z	wCV5Z	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ
SiS (¹ Σ ⁺)	aV(6+d)Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
N ₂ H ₂ (¹ A _g)	aV6Z	wCV5Z	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+
N ₂ H ₄ (¹ A)	aV5Z	wCV5Z	VTZ_DK	aVDZ/aVDZ	CCSDTQ(CV)/wCVDZ CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ+
CH ₂ Cl ₂ (¹ A ₁)	aV(6+d)Z(Cl)/ aV6Z(H,C)	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CH ₃ O methoxyl radical	aV6Z	wCVQZ	VTZ_DK	aCVTZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CH ₃ OH methanol	aV5Z	CVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CH ₃ CO (² A')	aV5Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ
C ₃ H ₈ <i>n</i> -propane	aV5Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ
PS (² Π)	aV(6+d)Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ
C ₂ H ₄ O oxirane	aV5Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDT(Q)/VDZ+ cf est. FCI/VDZ
C ₂ H ₄ O acetaldehyde	aV5Z	wCVQZ	VTZ_DK	aVDZ/aVDZ	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
C ₂ H ₂ O ketene	aV6Z	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VQZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
CH ₃ Cl (¹ A ₁)	aV(6+d)Z(Cl)/ aV6Z(H,C)	wCVQZ	VTZ_DK	aVTZ/aVDZ	CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
HCN (¹ Σ ⁺)	aV7Z	wCV5Z	VTZ_DK	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ +CCSDTQ5/VDZ+ cf est. FCI/VDZ+

TABLE II. (Continued.)

System	CCSD(T)(FC)	CCSD(T)(CV)	SR	ZPE ^a	HO correlation ^b
H ₂ SiO (¹ A ₁)	aV(6+d)Z(Si)/ aV6Z(H, O)	wCV5Z	VTZ_DK	VQZ+1	CCSDTQ(CV)/wCVDZ CCSDT/VTZ+ CCSDTQ/VDZ+ cf est. FCI/VDZ
SiH (² Π)	aV(6+d)Z(Si)/ aV6Z(H)	wCV5Z	VTZ_DK	Expt.	CCSDTQ/VQZ+ FCI/VTZ
K ₂ (¹ Σ _g ⁺)		awCV6Z	wCVQZ_DK	Expt.	CCSDT(CV)/wCVTZ+ CCSDTQ(CV)/wCVDZ+ cf est. FCI(CV)/wCVDZ
KF (¹ Σ ⁺)	awCV6Z/aV6Z	awCV5Z/ wCV5Z	wCVQZ_DK	Expt.	CCSDT(CV)/wCVTZ+ CCSDTQ(CV)/wCVDZ+ cf est. FCI(CV)/wCVDZ
I ₂ (¹ Σ _g ⁺)	aV6Z-PP+tightf	wCVQZ	None	Expt.	CCSDT/VQZ+ CCSDTQ/VTZ+ CCSDTQ5/VDZ+ cf est. FCI/VDZ+ CCSDTQ(CV)/wCVDZ

^aZPE basis set. "Expt." indicates that the ZPE is based on an experimental value. If two basis sets are indicated, the first was used in obtaining the harmonic frequencies and the second was used for the anharmonicities.

^bHO correlation correction, i.e., beyond CCSD(T). Unless otherwise noted, these corrections were carried out using the FC approximation.

^cInternally contracted, CAS CI/CBS value reported by Peterson *et al.* (Ref. 136).

^dHO CV correction taken from Karton *et al.* (Ref. 16). This is based on a CBS(ℓ_{\max}^3) extrapolation of the RCCSDT(CV)/cc-pCVQZ and RCCSDT(CV)/cc-pCVTZ results, plus a UCCSDT(Q)/cc-pCVTZ component.

^eAnharmonic zero point energy for CH₄ reported by Karton *et al.* (Ref. 15) and based on data published by Schwenke (Ref. 137) and adjusted for experimental minus calculated differences in the fundamental frequencies.

^fCCSD(T)/cc-pVQZ quartic force field value reported by J. M. L. Martin *et al.* (Ref. 84).

^gCCSD(T)(full)/cc-pVQZ result from Breidung *et al.* (Ref. 85).

would have been possible to apply one or more of the CBS extrapolation formulas in the case of the very smallest molecules, CCSDT and CCSDTQ calculations with the cc-pVTZ and cc-pVQZ basis sets rapidly become intractable for larger molecules.

An additional complication that arises when attempting to extrapolate the HO contribution is the opposing signs of the CCSD(T) → CCSDT and CCSDT → CCSDTQ corrections, observed in many chemical systems. Individually, the two corrections may be much larger than their sum, making it difficult to estimate the HO correction in the basis set limit to an accuracy of 0.1 kcal/mol. In particularly problematic cases, such as C₂ (¹Σ_g⁺), the CCSDT/CBS correction to the dissociation energy (−2.20 kcal/mol) and the CCSDTQ/CBS correction (2.29 kcal/mol) almost cancel.² Combining corrections obtained with different basis sets can easily lead to biased results if care is not taken. As an illustration, if one were to combine the C₂ CCSDT/CBS correction with the CCSDTQ/cc-pVDZ correction, the resulting HO correction (−0.54 kcal/mol) is in error by more than 0.5 kcal/mol and possesses the wrong sign. Similarly, combining CCSDT/cc-pVTZ and CCSDTQ/cc-pVDZ corrections leads to a smaller but still non-negligible error of 0.3 kcal/mol. With CCSDT/cc-pVQZ and CCSDTQ/cc-pVTZ corrections, the error drops to 0.1 kcal/mol. The same problem, i.e., combining large corrections of opposite signs, seldom arises with the FC and CV pieces. This makes it safer to perform CBS extrapolations on the CCSD(T)(FC) and CCSD(T)(CV) contributions to atomization energies since the result of the extrapolations are typically of the *same sign*. For example, in the case of H₂CO (¹A₁), FC CBS extrapolations produce a bind-

ing energy that is ~0.3 kcal/mol larger than the best raw CCSD(T)(FC)/aug-cc-pV7Z value. CBS extrapolation of the CV correction also produces an increase in the binding energy but only by ~0.02 kcal/mol.

Because the CCSDT correction is more sensitive to the quality of the basis set than the CCSDTQ correction, we have adopted the practice of combining CCSDT/cc-pV(*n*+2)Z and CCSDTQ/cc-pV(*n*+1)Z and CCSDTQ5/cc-pV*n*Z adjustments for many of the higher order corrections in the present work. In addition, we examined each molecule on a case-by-case basis in order to ascertain the need to reduce the uncertainty associated with the HO correction by performing larger basis set calculations when required and when permitted by our computational resources. When the system's size precluded larger calculations, we increased our estimate of the uncertainty arising from the HO component.

The largest CCSDTQ calculations performed for the present study (cyclopropane and acetaldehyde with the cc-pVDZ basis set) involved ~2.7 × 10⁹ configurations and required 20 days on two 2.8 GHz Opteron cores for each converged energy evaluation. Some of the systems included in our sample set were even larger than cyclopropane. For these systems, CCSDTQ calculations proved to be prohibitively expensive and necessitated the use of scaled CCSDT(Q) corrections instead. The largest CCSDT(Q) calculation, *n*-propane, C₃H₈, with the cc-pVDZ basis set, involved 5.0 × 10⁹ configurations. The scale factors were based on the CCSDTQ/CCSDT(Q) ratio for a related but smaller chemical system or on the ratio for the same system with a smaller basis set. For example, the scale factor for *n*-propane was adopted from ethane. In a limited number of comparisons,

CCSDT(Q) was found to slightly overestimate the contribution of iterative (connected) quadruple excitations, but the calculated ratios of the CCSDTQ and CCSDT(Q) valence correlation energies were >0.9999 .

Corrections to molecular structures and normal mode frequencies obtained from calculations beyond CCSDTQ are very expensive. In some cases, we were able to perform CCSDTQ5 and FCI calculations, as indicated in Table II. We also estimated the FCI limit through the use of a continued fraction (cf) approximant, originally formulated by Goodson⁸³ in terms of HF, CCSD, and CCSD(T) energies. Early tests against explicit FCI results showed the approximant based on this particular sequence of energies incapable of producing corrections to CCSD(T) that were consistently better than the uncorrected results.¹⁰ However, replacing the original sequence of energies with CCSD, CCSDT, and CCSDTQ energies significantly improves the reliability of the method, albeit at greatly increased computational cost.² Despite the improvement over the original formulation, the cf(CCSDTQ) approximation is not perfect, a conclusion that might be anticipated from such a simple extrapolation procedure. Consequently, whenever the cf approximant predicts a large correction to CCSDTQ, the findings should be viewed with caution and adopted with an understanding of the potential inaccuracies.

Karton *et al.*¹⁶ found the cf method to be of “limited” predictive power, pointing to F_2 ($^1\Sigma_g^+$) as an example where the method overestimated the quintuple contribution by a factor of 5. In order to further test the cf(CCSDTQ) extrapolation, we compared its performance against FCI and cf(CCSDTQ5) estimated FCI corrections to CCSDTQ atomization energies in Table III. In 42 out of 49 comparisons, the cf estimate improved the CCSDTQ value or correctly predicted that ΔFCI was <0.01 kcal/mol. The mean absolute error was 0.033 kcal/mol. Ozone (O_3) is a well-studied molecule with significant multiconfigurational character that might be expected to exhibit a substantial residual correlation even at the CCSDTQ level. The cf(CCSDTQ) correction to the CCSDTQ/cc-pVDZ atomization energy is 0.66 kcal/mol, compared to 0.49 kcal/mol obtained from a cf(CCSDTQ5) extrapolation. Karton *et al.*¹⁵ reported a CCSDTQ5/DZ+CCSDTQ5(6)/DZ correction for O_3 of 0.48 kcal/mol. Thus, while use of the cf(CCSDTQ) approximation for this molecule would result in an overestimation of the residual correlation correction, it nevertheless significantly reduces the error in the atomization energy. Karton *et al.* noted that a simple geometric extrapolation of CCSDT, CCSDTQ, and CCSDTQ5 energies was as effective as explicitly computing the CCSDTQ56 energy.

Failures of the cf approximation were characterized by large overestimates of the FCI or cf(CCSDTQ5) corrections, such as occurred with F_2 and HF. In light of practical considerations that currently limit the number of systems where CCSDTQ5 or FCI is possible, we judge the cf(CCSDTQ) approximation to be a viable alternative for estimating the effects of correlation recovery beyond CCSDTQ. When used with caution, it can be helpful in estimating the magnitude of the residual correlation error.

In a few cases, e.g., CF ($^2\Pi$), BF ($^1\Sigma^+$), and SiO ($^1\Sigma^+$),

we found the CCSDTQ5 total energy to be slightly higher than the CCSDTQ energy, perhaps hinting at a potential problem for any procedure that attempts to extrapolate the coupled cluster energy sequence. In cases where explicit FCI results were unavailable, cf(CCSDTQ5) estimates were substituted for the former. While the use of such high level energies is expected to result in a further improvement in the accuracy of the approximation, it was difficult to test because $E(\text{CCSDTQ5})$ was already very close to the FCI energy.

The contribution of correlation recovery beyond CCSD(T) for the CV correction is even more challenging than at the FC core level due to the rapid increase in the number of active electrons and the steep scaling of CCSDTQ. However, if very high accuracy is desired, i.e., on the order of 0.1 kcal/mol or better, some estimate of this effect may be required, judging by the limited available information. The W4.2 and W4.3 model chemistries¹⁵ contain a CV (T) \rightarrow T correction obtained with the cc-pCVTZ basis set. In our earlier study,² we reported CCSDTQ(CV) corrections to $D_e(C_2)$ of 0.12 and -0.02 kcal/mol from cc-pCVDZ and cc-pCVTZ(no *f*) basis sets. Subsequently, it was discovered that the latter value was computed incorrectly. The correct value is 0.11 kcal/mol. Both values are in reasonable agreement with the 0.18 kcal/mol correction reported by Karton *et al.*¹⁶ which was based on a $1/\ell_{\max}^3$ (cc-pCVTZ, cc-pCVQZ) CBS extrapolation of the (T) \rightarrow T component combined with an UCCSDT(Q)/cc-pCVTZ correction. Among the collection of small molecules considered by Karton *et al.*, most HO CV corrections were <0.05 kcal/mol. Only a few reached 0.1 kcal/mol or greater, with BN displaying the largest value (0.20 kcal/mol). Given the expense of HO CV corrections, we have adopted several of the values from the work of Karton *et al.*¹⁶ in the present results. In a few cases, we have determined HO CV corrections based on new CCSDTQ(CV)/cc-pwCVDZ calculations.

As time consuming as HO CV calculations are for molecules composed of first row elements, they become even more expensive for molecules with second and third row elements because of the rapid increase in the number of active electrons. A CV calculation on the fluorine atom adds only two electrons to the frozen core pool of 7 electrons, compared to 8 ($2s^22p^6$) for Cl and 18 ($3s^23p^63d^{10}$) for Br. As an illustration of the amount of computer time involved, a single energy evaluation at the CCSDTQ(CV)/cc-pwCVDZ level of theory for ClO ($^2\Pi$), which involved 440×10^6 configurations, required 4.5 days running on a single 2.8 GHz Opteron processor. Consequently, geometry optimizations were not attempted at the CCSDTQ(CV) level of theory. The energies were evaluated at the CCSD(T)(CV) and CCSD(T)(FC) optimized structures obtained with the same basis sets.

F. Zero point vibrational energies

In our previous studies, the zero point vibrational energies (ZPEs) were taken from a variety of sources, including (1) experiment,⁷⁸ (2) accurate quartic force field values,^{15,84–87} (3) an averaging of theoretical harmonic and experimental fundamental frequencies, and (4) CCSD(T)

TABLE III. CCSDTQ atomization energies, cf, and FCI corrections (kcal/mol) in small molecules (all open shell systems, including the atomic asymptotes, were based on ROHF wave functions).

System	Basis set	CCSDTQ $D_e/\Sigma D_e^a$	Δcf^b	ΔFCI^c	cf error	% ΔFCI^d
B ₂ (¹ Σ _g ⁻)	cc-pVDZ	59.64	0.112	0.077	0.035	145
	cc-pVTZ	64.27	0.140	0.109	0.031	128
C ₂ (¹ Σ _g ⁺)	cc-pVDZ	130.44	0.200	0.412	0.212	49
	cc-pVTZ+ ^e	139.18	0.282	0.407 ^f	0.125	68
N ₂ (¹ Σ _g ⁺)	cc-pVDZ	201.44	0.145	0.140	0.005	104
O ₂ (³ Σ _g ⁻)	cc-pVDZ	105.19	0.254	0.144 ^c	0.110	176
F ₂ (¹ Σ _g ⁺)	cc-pVDZ	28.19	0.191	0.057 ^d	0.134	316
NO (² Π)	cc-pVDZ	132.80	0.102	0.105 ^g	0.002	97
H ₂ O (¹ A ₁)	cc-pVDZ	209.16	0.044	0.011	0.033	400
	cc-pVDZ(H)/ cc-pVTZ(O)	216.28	0.008	0.007	0.001	114
HO ₂ (² A'')	cc-pVDZ	151.35	0.088	0.060 ^g	0.028	146
NH (³ Σ ⁻)	cc-pVDZ	71.61	0.003	0.002	0.001	150
OH (² Π)	cc-pVDZ	94.40	0.018	0.003	0.015	600
	cc-pVTZ	103.01	0.002	0.001	0.001	200
HF (¹ Σ ⁺)	cc-pVDZ	126.52	0.051	0.006	0.045	850
BN (³ Π)	cc-pVDZ	87.59	0.037	0.010	0.027	380
	cc-pVTZ	97.89	0.037	0.048 ^b	0.011	77
BP (³ Π)	cc-pVDZ	62.21	0.022	0.021	0.001	105
	cc-pVTZ	71.69	0.046	0.002 ^h	0.044	2300
CN (² Σ ⁺)	cc-pVDZ	160.36	-0.257	-0.199	0.058	130
CN ⁺ (² Σ ⁺)	cc-pVDZ	101.42 ⁱ	0.163	0.435	0.272	37
AlN (³ Π)	cc-pVTZ	52.60	0.058	0.078 ^h	0.020	74
CH ₂ (³ B ₁)	cc-pVDZ	177.60	0.002	0.002	0.000	100
CH ₂ (¹ A ₁)	cc-pVDZ	165.83	0.006	0.005	0.001	120
CH ₃ (² A ₂ '')	cc-pVDZ	287.62	0.005	0.005	0.000	100
O ₃ (¹ A ₁)	cc-pVDZ	116.33	0.662	0.486 ^g	0.176	136
C ₂ H ₂ (¹ Σ _g)	cc-pVDZ	371.71	0.057	0.103 ^g	0.046	60
CO (¹ Σ ⁺)	cc-pVDZ	242.04	0.049	0.039 ^g	0.010	125
H ₂ CO (¹ A ₁)	cc-pVDZ	345.79	0.129	0.116 ^g	0.013	112
NP (¹ Σ ⁺)	cc-pVDZ	116.10	0.243	0.249 ^g	0.006	98
CS (¹ Σ ⁺)	cc-pVDZ	154.10	0.033	0.058 ^g	0.020	57
FO (² Π)	cc-pVDZ	39.38	0.066	0.044 ^g	0.022	150
ClO (² Π)	cc-pVDZ	42.87	0.045	0.046 ^g	0.001	98
BrO (² Π)	cc-pVDZ	38.98	0.049	0.051 ^g	0.002	96
SiH ₂ (¹ A ₁)	cc-pVDZ	140.64	0.003	0.001	0.002	300
Al ₂ (³ Π _u)	cc-pVDZ	28.67	0.010	0.007	0.003	143
Si ₂ (³ Σ _g ⁻)	cc-pVDZ	61.94	0.034	0.037	0.003	92
P ₂ (¹ Σ _g ⁺)	cc-pVDZ	90.43	0.152	0.168	0.016	90
S ₂ (³ Σ _g ⁻)	cc-pVDZ	82.43	0.066	0.089 ^g	0.023	74
Cl ₂ (¹ Σ _g ⁺)	cc-pVDZ	42.13	0.030	0.029 ^g	0.001	103
SO (³ Σ _g ⁻)	cc-pVDZ	97.22	0.144	0.101 ^g	0.043	142
PS (² Π)	cc-pVDZ	80.01	0.054	0.075	0.021	72
HCl (¹ Σ ⁺)	cc-pVDZ	98.29	0.005	0.003	0.002	167
HCN (¹ Σ ⁺)	cc-pVDZ	283.38	0.100	0.130 ^g	0.030	77
HNC (¹ Σ ⁺)	cc-pVDZ	268.09	0.047	0.058 ^g	0.011	81
HI (¹ Σ ⁺)	cc-pVDZ	73.48	-0.002	0.002	0.004	-100
SiS (¹ Σ ⁺)	cc-pVDZ	127.61	0.040	0.006	0.034	667
Br ₂ (¹ Σ _g ⁺)	cc-pVDZ	37.78	0.022	0.023 ^g	0.001	96

TABLE III. (Continued.)

System	Basis set	CCSDTQ $D_e/\Sigma D_e^a$	Δ_{cf}^b	ΔFCI^c	cf error	% ΔFCI^d
$I_2 (^1\Sigma_g^+)$	cc-pVDZ	33.34	0.019	0.022 ^g	0.003	86
Av. ^j					0.033	

^aRCCSDTQ(FC) atomization energies.

^bAtomization correction based on a cf extrapolation of the CCSD, CCSDT, and CCSDTQ energies. A positive value indicates an increase in the atomization energy.

^cFCI corrections to the CCSDTQ atomization energies.

^d $(\Delta_{cf}/\Delta FCI) \times 100$.

^eIncludes diffuse *s* and *p* functions.

^fFCI energy taken from Gan and Harrison (Ref. 194).

^gFCI correction based on a cf extrapolation of the CCSDT, CCSDTQ, and CCSDTQ5 energies.

^hFCI energy taken from Gan *et al.* [Ref. 81(b)].

ⁱCN⁺ dissociates to C⁺(²P)+N(²D). However, the ²D state of nitrogen requires a two configuration zeroth order description and was, thus, not amenable to a single configuration coupled cluster approach. For this comparison, we used the ⁴S ground state energy of nitrogen.

^jBased on 49 comparisons.

harmonic frequencies. The extent to which uncertainty in the ZPE contributes to the overall uncertainty in the final heat of formation is often overlooked. We have stressed the importance of this component, stating that it could “potentially be one of the leading sources of error in the calculation of accurate heats of formation.”⁸ A recent study of ethane by Karton *et al.*⁸⁸ reinforces the same point. As the chemical system and the size of the ZPE both increase, it becomes increasingly difficult to prevent the uncertainty associated with the vibrational energy calculation from simultaneously growing. For example, in a coupled cluster study of the heats of formation of the *n*-alkanes, the ZPE of *n*-octane was reported to be ~ 152 kcal/mol.¹² Computing this quantity accurate to within 1 kcal/mol (0.6%), the accepted threshold for chemical accuracy, is a formidable challenge.

All of the newly determined ZPEs used in this study incorporated anharmonic corrections and were based on the expression

$$ZPE = 0.5(ZPE_H + ZPE_F) + \chi_0 - 0.25(\sum \chi_{ii}), \quad (1)$$

where $ZPE_H = 0.5(\sum \omega_i)$ and $ZPE_F = 0.5(\sum \nu_i)$.⁸⁹ Anharmonic corrections were obtained from FC, second order Møller–Plesset perturbation theory, MP2(FC), calculations with GAUSSIAN 03,³⁵ which includes a second order perturbative treatment of such effects using finite difference evaluations of third and semidiagonal fourth derivatives. The harmonic frequencies were obtained at the CCSD(T)(FC) level of theory with the same aug-cc-pV*n*Z basis set sequence used in determining atomization energies and molecular structures, as indicated in Table II.

On a practical level, estimating the degree of convergence in a polyatomic molecule’s ZPE can present as great a computational challenge as estimating the uncertainty in the other pieces contributing to the zero-point-inclusive atomization energies (D_0 and ΣD_0) or heats of formation. This is partially due to the lack of CCSD(T)(FC) analytical first and second derivatives in many electronic structure packages, including MOLPRO. Our approach to the problem has evolved over time. Ideally, it should be consistent with the approach to analyzing error in the computed atomization energies and molecular structures. To the extent possible, each of the con-

tributions to the ZPE is scrutinized with respect to convergence in the one-particle and *n*-particle expansions. Table IV illustrates theory’s ability to reproduce the harmonic frequencies of first row diatomics, such as CH and CO. In the case of CH, the comparatively large contribution from the diagonal Born–Oppenheimer correction (DBOC) (see next section) to ω_e is consistent with the findings of Valeev and Sherrill for BH.⁹⁰ The DBOC represents a first order correction to the electronic energy due to the motion of the nuclei.

On the basis of the diatomic harmonic frequency data contained in the CRDB and the results in Table IV, it appears likely that the inclusion of a CV correction to the zero point energy, without compensating corrections from SR, HO, and in some cases a DBOC, can lead to skewed results. This assumes that stretching contributions to the ZPE dominate the contributions from other modes, e.g., rocks, wags, and twists. If only the CV correction is considered, the resulting

TABLE IV. A comparison of theoretical and experimental harmonic frequencies (cm⁻¹).

System	Component	
CH (² Π)	R/UCCSD(T)(FC)/CBS ^a	2857.6
	R/UCCSD(T)(CV)/CBS ^b correction	8.6
	R/UCCSD(T)-DK(FC)/cc-pVQZ_DK correction	-1.1
	RCCSDT(FC)/cc-pVQZ correction	-2.8
	RCCSDTQ(FC)/cc-pVTZ correction	-0.1
	FCI(FC)/cc-pVDZ correction	0.0
	DBOC CISD(FC)/aug-cc-pVTZ	-1.9
	Total	2860.2
	Expt. ^c	2858.5
	CO (¹ Σ ⁺)	CCSD(T)(FC)/CBS ^a
CCSD(T)(CV)/CBS ^b correction		10.2
CCSD(T)-DK(FC)/cc-pVQZ_DK correction		-0.9
CCSDT(FC)/cc-pVQZ correction		2.5
CCSDTQ(FC)/cc-pVTZ correction		-8.0
Total		2169.5
Expt. ^c		2169.8

^aBased on aug-cc-pVQZ through aug-cc-pV6Z basis sets.

^bBased on cc-pwCVTZ through cc-pwCV5Z basis sets.

^cExperimental ω_e value from Huber and Herzberg (Ref. 78).

^dBased on aug-cc-pV5Z through aug-cc-pV7Z basis sets.

TABLE V. Contributions to the ZPVE of small molecules (kcal/mol) (basis set notation follows the same pattern defined in Table I, i.e., aVDZ=aug-cc-pVDZ, etc.).

System	FC					CV	
	Level	$0.5\sum\omega_i$	Level	Anharm. Δ	Total	Level	CV Δ
NH ₂	CCSD(T)/aVDZ	11.82	MP2/aVDZ	-0.18	11.64	CCSD(T)(CV)/wCVDZ	0.01
	CCSD(T)/aVTZ	11.94	MP2/aVDZ	-0.18	11.76	CCSD(T)(CV)/wCVTZ	0.02
	CCSD(T)/aVQZ	11.99	MP2/aVTZ	-0.18	11.81	CCSD(T)(CV)/wCVQZ	0.02
	CCSD(T)/CBS	12.02	MP2/aVTZ	-0.18	11.84		
H ₂ CO	CCSD(T)/aVDZ	16.58	MP2/aVDZ	-0.23	16.35	CCSD(T)(CV)/wCVDZ	0.02
	CCSD(T)/aVTZ	16.67	MP2/aVDZ	-0.23	16.44	CCSD(T)(CV)/wCVTZ	0.03
	CCSD(T)/aVQZ	16.71	MP2/aVTZ	-0.22	16.49	CCSD(T)(CV)/wCVQZ	0.04
	CCSD(T)/CBS	16.74	MP2/aVTZ	-0.22	16.52		
C ₂ H ₄	CCSD(T)/aVDZ	31.67	MP2/aVDZ	-0.44	31.23	CCSD(T)(CV)/wCVDZ	0.04
	CCSD(T)/aVTZ	31.75	MP2/aVDZ	-0.44	31.31	CCSD(T)(CV)/wCVTZ	0.07
	CCSD(T)/aVQZ	31.89	MP2/aVTZ	-0.25	31.64	CCSD(T)(CV)/wCVQZ	0.08
	CCSD(T)/CBS	31.91	MP2/aVTZ	-0.25	31.66		
C ₂ H ₆	CCSD(T)/aVDZ	46.46	MP2/aVDZ	-0.66	45.80	CCSD(T)(CV)/wCVDZ	0.06
	CCSD(T)/aVTZ	46.87	MP2/aVDZ	-0.66	46.21	CCSD(T)(CV)/wCVTZ	0.09
	CCSD(T)/aVQZ ^a	46.90	MP2/aVTZ	-0.67	46.23		

^aEstimated by applying the cc-pVTZ→cc-pVQZ change to the aug-cc-pVTZ set of harmonic frequencies.

ZPE is likely to be overestimated. In their study of ethane, Karton *et al.*⁸⁸ commented that their final ZPE, which included a CV correction but no SR or HO corrections might be “on the order of 0.05 kcal/mol too high.” The situation with vibration energies in many ways parallels the situation with atomization energies. The largest contribution comes from estimating the harmonic value at something approaching the CCSD(T)(FC) CBS limit, followed by a number of corrections of differing signs that may largely cancel but nevertheless need to be included for very high accuracy studies.

Table V shows a breakdown of the various contributions to ZPEs in four small polyatomic molecules. For these systems, the CCSD(T)(FC) harmonic component increases monotonically with increasing basis set size. With the smallest basis set (aug-cc-pVDZ), the values are from 1% to 2% smaller than the CBS limit. To the extent this finding transfers to larger systems, a ZPE for octane, for example, that was determined at the CCSD(T)(FC)/aug-cc-pVDZ level of theory could conceivably be ~1.5 kcal/mol smaller than the basis set limit. At the present state of the art, it should be possible to compute a reasonably accurate anharmonic correction for a system the size of octane using density functional theory or MP2, but CV, DBOC, and HO corrections are currently prohibitively expensive, even though they could potentially change the ZPE by 0.5–1.0 kcal/mol.

The MP2 anharmonicity corrections in Table V show little sensitivity to the quality of the basis set, except in the case of ethylene. The CV correction is equally insensitive. We consider the current ZPEs, *excluding* the CV corrections, to be our best values. While we could not afford to perform a sensitivity analysis for every polyatomic molecule in our list, the uncertainties in our vibrational energies could conservatively contribute another 0.1–0.3 kcal/mol to the overall uncertainties in the final heats of formation. A comparison with literature values obtained from CCSD(T) quartic force fields shows generally good agreement. For example, for

H₂CO (¹A₁) we determined a ZPE of 16.52 kcal/mol, using CCSD(T)(FC)/CBS harmonic frequencies and MP2(FC)/aug-cc-pVTZ anharmonicities, compared to the CCSD(T) quartic force field value of 16.53 kcal/mol reported by Martin *et al.*⁸⁶ The latter was based on CCSD(T)(FC)/cc-pVQZ harmonic frequencies and CCSD(T)(FC)/cc-pVTZ anharmonicities. For ethylene, our 31.66 kcal/mol compares to a value of 31.38 kcal/mol using a CCSD(T)(FC)/cc-pVTZ quartic force field.⁹¹ A discussion of the sometimes counterbalancing effects of HO correlation, SR corrections, and CV effects for first row diatomics was given by Martin.⁹²

G. Diagonal Born–Oppenheimer corrections

For molecules composed of light elements, such as hydrogen, the commonly employed Born–Oppenheimer approximation, which separates electronic and nuclear motions, introduces a potentially significant error into the calculation of molecular properties when judged by the goals of high accuracy studies. In the present work, the majority of DBOC corrections were obtained from HF/aug-cc-pVTZ calculations using a development version of PSI3.⁹³ These corrections were evaluated at HF/aug-cc-pVTZ geometries optimized without inclusion of the DBOC. As an illustration of the magnitude of this component, Fig. 3 shows the growth of the DBOC to the atomization energy of the *n*-alkanes as a function of the number of carbon atoms. For the smaller alkanes, the growth appears to be nearly linear. If this trend continued, the HF correction for decane (C₁₀H₂₂) would be expected to exceed 0.5 kcal/mol. Karton *et al.* reported a DBOC to the atomization energy of benzene of 0.24 kcal/mol.¹⁵ On the other hand, for small molecules composed entirely of heavier first and second row elements, such as N₂ or P₂, the DBOCs are small (≪0.05 kcal/mol) and can probably be neglected in all but the highest accuracy studies.

In most cases, the DBOC to the atomization energy is

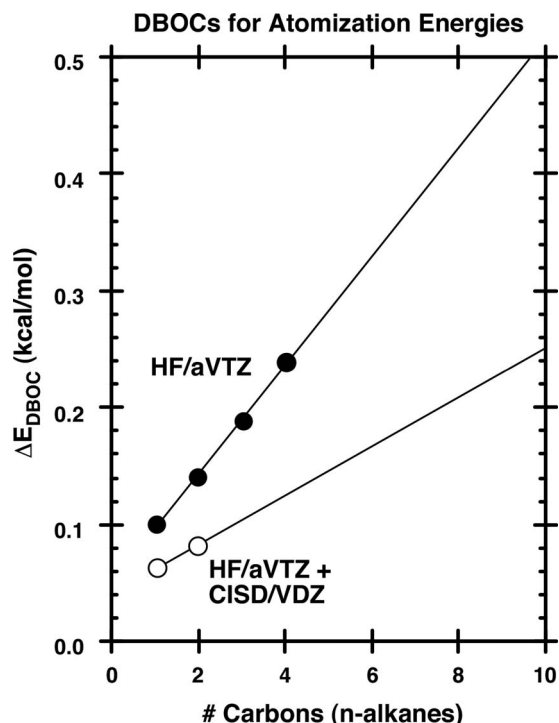


FIG. 3. Growth of the DBOC to the atomization energies of the n -alkanes (kcal/mol).

relatively insensitive to the quality of the basis set or the inclusion of correlation effects.^{90,94} Restricted Hartree–Fock (RHF) and configuration interaction singles and doubles (CISD) wavefunction comparison calculations were performed on a number of small molecules, including H_2 , LiH, HO_2 , H_2O , CH, CH_2 , CH_3 , N_2 , and CS. The differences were small in an absolute sense. In the worst case (H_2), the CISD (FCI for this two-electron system) correction to the RHF DBOC was -0.04 kcal/mol. These results are consistent with the findings of Karton and Martin for P_2 and P_4 , who reported CISD corrections of just 0.003 and 0.001 kcal/mol, respectively.⁹⁵ However, as the chemical system increases in size and includes more hydrogens, the differences between HF and correlated values increases correspondingly, as indicated in Fig. 2. For example, Gauss *et al.*⁹⁴ reported a RHF \rightarrow CCSD correction of 0.09 kcal/mol for 1,3-butadiene. Thus, we tentatively assume that the use of HF DBOCs increases the uncertainty in our atomization calculations for this particular set of molecules by ≤ 0.1 kcal/mol. When available, we have adopted the CCSD(CV)/aug-cc-pCVQZ values recently reported by Harding *et al.*¹⁷

III. RESULTS AND DISCUSSION

A. Atomization energies

The individuality of molecules and the subtle differences among even similar appearing compounds is what makes chemistry such an intellectually rich and rewarding field. That individuality is reflected in Table VI, where the various contributions to zero-point-inclusive atomization energies are summarized. What is obvious from even a casual glance at the data is the wide variation in magnitude of the corrections. What is not revealed in Table VI is the variation in

basis set sensitivity for the individual components. For example, the CV correction for CO_2 is ~ 1.8 kcal/mol and increases by 0.3 kcal/mol as the basis set is increased from cc-pwCVTZ to the CBS limit, whereas the same correction for O_3 is nearly three orders of magnitude smaller, of opposite sign, and barely changes over the same span of basis sets. The HO correction, designated as ΔE_{HO} in Table VI, ranges from being completely negligible to exceeding 3 kcal/mol in the case of O_3 and FOO, two systems known to cause problems for single reference coupled cluster theory. This variability makes drawing general conclusions difficult and is one reason why we prefer our flexible approach which takes into account the specific needs of each molecule.

Together with the energy contributions, values of the T_1 diagnostic obtained with the largest CCSD(T)(FC) basis set at the respective optimized geometries are included in Table VI. For coupled cluster calculations, Lee *et al.* proposed this ratio as a measure of the extent of “nondynamical” correlation present in a system.^{96,97} Other metrics have also been suggested, such as the D_1 and D_2 diagnostics.^{97,98} Karton *et al.*¹⁵ discussed the use of the total atomization energy (TAE) recovered by the quasiperturbative (T) step and given simple numeric guidelines, e.g., $\%TAE(T) \leq 2\%$ indicates little nondynamical effect, whereas $\%TAE(T)$ of 4%–5% indicates moderate nondynamical correlation. Inclusion of the T_1 values in Table VI was not meant to endorse this choice over the others but is intended to provide a convenient, qualitative measure of the likely quality of the CCSD and CCSD(T) results.

Because of the small size of the molecules chosen for this study, it is inevitable that many of them have been the subject of numerous previous studies. A comprehensive review of previous studies involving any of the molecules from our list was considered beyond the scope of this work and has not been attempted. Instead, we will mention only those studies that offer some particularly salient feature that touches on the present discussion. If results were available which were too expensive to recompute, we have incorporated them in our best estimate. For example, two of the contributions to the HO correction for hydrogen peroxide, H_2O_2 , were obtained from Kállay and Gauss.^{80,99} These include a CCSDTQ(FC)/cc-pVTZ calculation, involving 3.7×10^9 configurations, and a CCSDTQ5(FC)/cc-pVDZ calculation, involving 1.3×10^9 configurations. The former required 8.5 days/iteration on a 3.4 GHz processor.

Theoretical and experimental heats of formation at 298.15 K are provided in Table VII. Because many of the molecules in this table have been the subject of multiple experimental studies over the years, numerous values are available in the literature. In an effort to avoid having Table VII become too unwieldy, we have selected what we consider to be the single best experimental value available. Many of the “experimental” values in Table VII are interim benchmark values extracted from the ATcT using the Core (Argonne) Thermochemical Network Version 1.064 (Refs. 72 and 100) and listed by Harding *et al.*¹⁷ We note that the ATcT values may actually incorporate accurate theoretical data, but for the sake of brevity we consider them simply as experimental measurements.

TABLE VI. Contributions to zero-point-inclusive atomization energies (kcal/mol).

System	CCSD(T) CBS FC ^a $D_e/\Sigma D_e$	T_1	CCSD(T) CBS CV ΔE_{CV}	ΔE_{SR}	ΔE_{HO}	DBOC	SO	ZPE	Best estimate $D_0/\Sigma D_0$
H ₂	109.48	0.0057	NA	NA	NA	0.01 ^c	NA	-6.21	103.27 ± 0.02
LiH	NA	0.0072	58.11	-0.02	0.01	-0.03	NA	-1.99	56.08 ± 0.3
Li ₂	NA	0.0205	24.49	<0.00	NA	<0.00	NA	-0.50	23.99 ± 0.3
HCl	107.39	0.0067	0.04	-0.24	0.02	0.04	-0.83	-4.24	102.15 ± 0.2
HBr	93.68	0.0067	0.54	-0.61	-0.02	0.04	-3.41	-3.75	86.47 ± 0.2
HI	79.54	0.0083	0.70	NA ^b	0.07	0.03	-6.74	-3.27	70.33 ± 0.2
ClO	64.56	0.0047	0.06	-0.20	0.66	0.00	-0.61	-1.22	63.25 ± 0.3
HOCl	165.84	0.0111	0.13	-0.30	0.09	0.07	-1.06	-8.18	156.59 ± 0.4
BeH	50.11	0.0138	0.51	-0.02	0.14	-0.04	0.00	-2.92	47.78 ± 0.2
BH	84.71	0.0141	0.19	-0.02	0.05	-0.11	-0.03	-3.35	81.44 ± 0.1
B ₂	65.17	0.0399	0.77	-0.06	1.82	0.01	-0.06	-1.50	66.15 ± 0.2
B ₂ H ₆	603.69	0.0103	2.91	-0.18	0.16	0.04	-0.06	-39.23	567.33 ± 0.6
BN	103.77	0.1080	1.07	-0.13	1.02	0.02	-0.03	-2.16	103.56 ± 0.3
BO	193.86	0.0241	1.53	-0.23	0.16	0.02	-0.25	-2.69	192.40 ± 0.3
BF	181.78	0.0152	0.71	-0.16	-0.03	0.01	-0.39	-2.00	179.92 ± 0.2
BP	77.10	0.0296	0.92	-0.17	0.84	0.01	-0.03	-1.55	77.12 ± 0.2
BCl	122.75	0.0159	0.33	-0.11	0.04	0.01	-0.87	-1.20	120.95 ± 0.3
CH	83.89	0.0091	0.14	-0.04	0.20	-0.10 ^c	-0.04	-4.04	79.99 ± 0.1
CH ₂ (³ B ₁)	189.85	0.0122	0.82	-0.15	0.02	0.01 ^c	-0.08	-10.55	179.92 ± 0.2
CH ₂ (¹ A ₁)	180.68	0.0096	0.39	-0.09	0.34	-0.15 ^c	-0.08	-10.29	170.80 ± 0.2
CH ₃	306.71	0.0062	1.07	-0.17	0.06	0.02 ^d	-0.08	-18.55	289.06 ± 0.2
CH ₄	419.14	0.0082	1.26	-0.19	0.01	0.05 ^d	-0.08	-27.74	392.45 ± 0.2
NH	82.85	0.0067	0.11	-0.07	0.11	-0.06 ^f	0.00	-4.64	78.30 ± 0.2
NH ₂	182.00	0.0122	0.32	0.08	0.12	-0.03 ^f	0.00	-11.84	170.65 ± 0.2
NH ₃	297.20	0.0080	0.65	-0.25	0.07	0.14	0.00	-21.33	276.48 ± 0.3
OH	107.06	0.0151	0.14	-0.13	0.05	0.00 ^f	-0.11	-5.29	101.72 ± 0.1
HF	141.59	0.0088	0.17	-0.20	-0.04	0.06	-0.38	-5.86	135.34 ± 0.2
C ₂	145.22	0.0389	0.98	-0.17	0.64	0.03 ^c	-0.17	-2.64	143.89 ± 0.3
C ₂ H	263.54	0.0166	2.11	-0.28	0.32	0.02 ^f	-0.17	-8.72	256.82 ± 0.2
C ₂ H ₂	402.78	0.0136	2.47	-0.29	0.14	0.08 ^f	-0.17	-16.50	388.51 ± 0.3
C ₂ H ₄	561.51	0.0113	2.36	-0.33	-0.03	0.12	-0.17	-31.66	531.80 ± 0.4
C ₂ H ₆	710.50	0.0083	2.42	-0.39	-0.03	0.07 ^d	-0.17	-46.23	666.17 ± 0.3
C ₃ H ₆	850.08	0.0081	3.72	-0.58	-0.20	0.18	-0.25	-50.29	802.66 ± 0.9
C ₄ H ₆	1007.87	0.0117	4.78	-0.66	0.12	0.11 ^e	-0.33	-52.12	959.77 ± 1.1
HOF	157.98	0.0131	0.11	-0.21	0.37	0.03	-0.61	-8.57	149.10 ± 0.3
HCO	277.94	0.0251	1.16	-0.28	0.29	-0.05 ^f	-0.31	-8.09	270.66 ± 0.3
H ₂ CO	373.15	0.0150	1.30	-0.34	0.10	-0.03	-0.31	-16.52	357.35 ± 0.3
CO	258.59	0.0176	0.95	-0.16	0.15	0.02	-0.30	-3.09	256.16 ± 0.3
CO ₂	388.12	0.0174	1.77	-0.48	0.26	0.04 ^f	-0.53	-7.24	381.94 ± 0.4
CF	132.33	0.0520	0.32	-0.16	0.10	0.01	-0.36	-1.86	130.38 ± 0.2
CF ₂	258.10	0.0166	0.42	-0.32	0.35	0.02	-0.85	-4.34	253.38 ± 0.3
CF ₃	345.05	0.0150	1.01	-0.65	0.24	0.00	-1.24	-7.66	336.75 ± 0.4
CN	179.20	0.0520	1.10	-0.16	0.99	0.01	-0.08	-2.95	178.11 ± 0.3
C ₂ N ₂	497.59	0.0152	3.46	-0.47	0.70	0.00	-0.17	-9.75	491.36 ± 0.6
CS	170.93	0.0246	0.75	-0.16	0.45	-0.03	-0.64	-1.83	169.47 ± 0.3
CS ₂	278.43	0.0195	1.47	-0.60	-0.09	0.01	-1.20	-4.30	273.72 ± 0.4
OCS	333.88	0.0186	1.59	-0.52	0.28	0.03	-0.86	-5.69	328.71 ± 0.4
NO	151.77	0.0213	0.42	-0.19	0.47	0.01	-0.04	-2.71	149.73 ± 0.3
HNO	204.93	0.0155	0.42	-0.27	0.63	-0.09 ^f	-0.22	-8.56	196.84 ± 0.3

TABLE VI. (Continued.)

System	CCSD(T) CBS FC ^a $D_e/\Sigma D_e$	T_1	CCSD(T) CBS CV ΔE_{CV}	ΔE_{SR}	ΔE_{HO}	DBOC	SO	ZPE	Best estimate $D_0/\Sigma D_0$
N ₂	227.14	0.0135	0.80	-0.14	0.43	0.01	0.00	-3.36	224.88 ± 0.3
NF	77.00	0.0237	0.06	-0.13	0.43	0.01	-0.39	-1.63	75.35 ± 0.3
NF ₂	144.99	0.0206	0.01	-0.23	0.66	0.01	-0.77	-3.75	140.92 ± 0.3
NF ₃	205.12	0.0156	-0.04	0.32	0.04	0.03	-1.16	-6.42	197.89 ± 0.7
NP	145.11	0.0172	0.89	-0.19	0.79	0.01	0.00	-1.91	144.70 ± 0.4
N ₂ O	268.66	0.0196	1.18	-0.46	0.99	-0.04	-0.22	-6.81	263.30 ± 0.4
NO ₂	225.85	0.0250	0.70	-0.43	1.35	0.00	-0.45	-5.40	221.62 ± 0.3
O ₂	119.90	0.0076	0.24	-0.17	0.64	0.01	-0.45	-2.25	117.92 ± 0.2
O ₃	144.29	0.0271	-0.02	-0.24	3.19	-0.01	-0.67	-4.15	142.39 ± 0.4
F ₂	38.43	0.0121	-0.11	-0.02	0.67	0.00	-0.77	-1.30	36.90 ± 0.2
F ₂ O	92.93	0.0159	-0.16	-0.09	1.18	0.01	-0.99	-3.34	89.54 ± 0.3
H ₂ O	232.67	0.0090	0.38	-0.27	-0.02	0.10	-0.22	-13.26	219.38 ± 0.2
H ₂ O ₂	268.32	0.0116	0.36	-0.37	0.28	0.12	-0.45	-16.44	251.82 ± 0.3
FO	52.17	0.0292	-0.05	-0.06	0.78	0.00	-0.34	-1.48	51.02 ± 0.2
FOO	131.55	0.0430	-0.01	-0.16	3.22	0.00	-0.82	-3.59	130.19 ± 0.3
PH ₃	241.65	0.0141	0.33	-0.44	0.13	0.02	0.00	-14.44	227.25 ± 0.3
P ₂	115.85	0.0172	0.77	-0.25	0.65	0.00	0.00	-1.11	115.91 ± 0.4
S ₂	103.52	0.0090	0.34	-0.28	0.33	0.00	-1.12	-1.04	101.75 ± 0.3
SO	125.73	0.0240	0.41	-0.31	0.19	0.01	-0.78	-1.63	123.62 ± 0.3
SO ₂	259.14	0.0202	0.92	-0.78	0.54	0.02	-1.01	-4.38	254.45 ± 0.6
SO ₃	345.36	0.0175	1.04	-1.76	0.26	0.04	-1.23	-7.80	335.91 ± 0.8
ClF	62.61	0.0120	-0.10	-0.16	0.28	0.00	-1.23	-1.12	60.28 ± 0.3
BrO	58.79	0.0053	-0.01	-0.72	0.84	0.00	-2.05 ^e	-1.05	55.80 ± 0.3
BrF	64.11	0.0124	-0.31	-0.59	0.30	0.00	-3.90	-0.96	58.65 ± 0.3
BrCl	56.52	0.0085	0.05	-0.35	-0.03	0.00	-3.94 ^b	-0.63	51.62 ± 0.3
Cl ₂	59.87	0.0088	-0.13	-0.14	0.11	0.00	-1.68	-0.80	57.23 ± 0.3
Br ₂	52.78	0.0083	0.29	-0.54	0.03	0.00	-6.71	-0.46	45.39 ± 0.3
SiO	191.77	0.0241	0.95	-0.26	-0.06	0.01	-0.64	-1.78	189.99 ± 0.3
HS	87.53	0.0083	0.07	-0.18	0.07	0.00	0.01	-3.81	83.69 ± 0.2
H ₂ S	183.51	0.0107	0.24	-0.38	0.07	0.05	-0.55	-9.40	173.54 ± 0.2
Si ₂	75.95	0.0242	0.13	-0.16	0.62	0.00	-0.85	-0.73	74.96 ± 0.3
HO ₂	174.70	0.0370	0.25	-0.27	0.53	<0.00	-0.45	-8.85	169.91 ± 0.2
ClCN	283.30	0.0139	1.59	-0.44	0.14	0.04	-0.92	-5.33	278.38 ± 0.5
HONO	311.05	0.0210	0.55	-0.41	1.06	0.08	-0.45	-12.49	299.39 ± 0.7
Al ₂	33.30	0.0241	-0.16	-0.11	0.64	0.00	-0.43	-0.41	32.83 ± 0.2
PO	142.65	0.0245	0.70	-0.30	0.31	0.01	0.10	-1.98	141.49 ± 0.4
FS	84.79	0.0171	0.09	-0.22	0.06	0.00	-0.42	-1.20	83.10 ± 0.2
CF ₂ O	419.10	0.0138	1.36	-0.67	0.30	0.06	-1.07	-8.78	410.30 ± 0.5
CH ₂ F ₂	436.88	0.0111	1.08	-0.54	0.06	0.07	-0.85	-20.46	416.24 ± 0.3
SiS	146.98	0.0201	0.50	-0.27	0.20	0.01	-0.99	-1.07	145.36 ± 0.2
N ₂ H ₂	295.20	0.0126	0.75	-0.32	0.38	0.03	0.00	-17.41	278.63 ± 0.4
N ₂ H ₄	436.87	0.0090	1.14	-0.51	0.20	0.17	0.00	-32.68	405.19 ± 0.6
CH ₂ Cl ₂	370.65	0.0087	1.00	-0.54	-0.32	0.06	-1.76	-18.35	350.74 ± 0.5
CH ₃ O	398.99	0.0206	1.30	-0.33	0.22	0.02	-0.31	-23.37 ^l	376.52 ± 0.3
CH ₃ OH	511.83	0.0096	1.34	-0.46	0.08	0.12	-0.31	-31.72	480.88 ± 0.6
CH ₃ CO	579.42	0.0214	2.44	-0.47	0.14	0.10	-0.39	-26.68	554.56 ± 0.8
C ₃ H ₈	1003.96	0.0085	3.60	-0.58	-0.11	0.10	-0.25	-63.77	942.95 ± 0.9
PS	103.94	0.0253	0.50	-0.28	0.45	0.00	-0.56	-1.05	103.00 ± 0.3
C ₂ H ₄ O ox.	648.73	0.0109	2.48	-0.56	0.09	0.12	-0.39	-35.55	614.92 ± 0.9

TABLE VI. (Continued.)

System	CCSD(T) CBS FC ^a $D_e/\Sigma D_e$	T_1	CCSD(T) CBS CV ΔE_{CV}	ΔE_{SR}	ΔE_{HO}	DBOC	SO	ZPE	Best estimate $D_0/\Sigma D_0$
C ₂ H ₄ O ac.	674.79	0.0141	2.60	-0.53	0.01	0.05	-0.39	-33.76	642.77 ± 0.8
C ₂ H ₂ O	530.28	0.0163	2.77	-0.48	0.16	0.10	-0.39	-19.41	513.03 ± 0.8
CH ₃ Cl	394.83	0.0079	1.11	-0.41	-0.15	0.07	-0.92	-23.19	371.34 ± 0.4
HCN	311.37	0.0145	1.67	-0.23	0.27	0.05 ^f	-0.08	-9.95	303.14 ± 0.3
H ₂ SiO	305.18	0.0201	0.37	-0.78	0.33	0.01	-0.65	-11.53	292.93 ± 0.4
SiH	73.80	0.0132	-0.07	-0.10	0.02	-0.05	-0.23	-2.89	70.48 ± 0.2
K ₂	NA	0.0196	12.60 ^j	-0.01	0.14	0.00	0.00	-0.13	12.60 ± 0.1
KF	NA	0.0121	119.03 ^k	-0.52	0.11	0.00	-0.39	-0.61	117.62 ± 0.3
I ₂	47.85 ^b	0.0088	0.68	0.09 ⁱ	-0.02	0.00	-12.87	-0.31	35.42 ± 0.3

^aFC, vibrationless CCSD(T) CBS atomization energy. The R/U method was used for open shell systems.

^bIncludes a 0.22 kcal/mol correction for the error associated with the pseudopotential, based on second and third order DK all-electron calculations with an aug-cc-pV5Z-DK basis set, as reported by Shepler *et al.* (Ref. 79).

^cCISD(FC)/aug-cc-pVTZ.

^dHF/aug-cc-pVTZ plus a CISD(FC)/cc-pVDZ correction taken from Karton *et al.* (Ref. 88).

^eCCSD(CV)/aug-cc-pCVTZ value from Gauss *et al.* (Ref. 94).

^fCCSD(CV)/aug-cc-pCVQZ value from Harding *et al.* (Ref. 17). For comparison purposes, the CISD(FC)/aug-cc-pVTZ values are NH=-0.06, NH₂=0.00, OH=0.00, C₂H₂=0.09; HCN=0.05 kcal/mol.

^gBrO SO correction based on the CAS, multireference CISD value reported by Peterson *et al.* (Ref. 52).

^hBrCl SO correction based on the natural orbital, multireference CIS value reported by Schepler and Peterson. (Ref. 61).

ⁱLamb shift correction taken from Shepler *et al.* (Ref. 79).

^jIncludes a 0.03 kcal/mol correction due to reducing the FC definition to the K (1s) orbitals.

^k Includes a 0.18 kcal/mol correction due to reducing the FC definition to the K (1s) orbitals.

^lSpin-vibronic zero point energy from Marenich and Boggs (Ref. 121).

Theoretical heats of formation at 0 K were converted to 298.15 K by applying temperature conversion factors based on standard thermodynamic and statistical mechanics expressions within the rigid-rotor/harmonic oscillator approximation.¹⁰¹ Temperature corrections for the atoms were taken from Curtiss *et al.*¹⁰² Vibrational frequencies, SO splittings, and electronic excitation energies for low-lying states were taken from the best available theoretical values.¹⁰³ Experimental values for the latter two properties were substituted in a few cases where theoretical values were unavailable. The excitation energies were typically obtained from multireference CI calculations. In most cases, the present conversion factors fell within 0.1 kcal/mol of the values reported in the compilations of experimental data, such as NIST-JANAF or the TRC Data Series tables.¹⁰⁴ However, the need for accurate vibrational frequencies as a function of the vibrational number for very low frequency modes, knowledge of the low-lying, electronic excited states, and consideration of the contribution from internal molecular motions such as inversion or internal rotation means that computing temperature conversions with an accuracy of ±0.1 kcal/mol is not an entirely trivial exercise.

The theoretical values in Table VII depend on the 0 K heats of formation of the corresponding elements. Except where noted, these were taken from the NIST-JANAF tables.¹⁰⁵ Uncertainties for several elements require additional comment. For gaseous boron, the NIST-JANAF tables gives $\Delta H_f^0(0 \text{ K}, \text{B}) = 132.7 \pm 2.9$ kcal/mol,¹⁰⁵ compared to the CODATA value of 133.8 ± 1.2 kcal/mol,¹⁰⁶ which is the same value listed in the compilation of Glushko *et al.*¹⁰⁷ and by Nordine and Schiffman.¹⁰⁸ Mar and Bedford reported val-

ues ranging from 132.9 ± 0.6 to 134.1 ± 2.6 kcal/mol.¹⁰⁹ Finally, Storms and Mueller recommend a much larger value of 136.2 ± 0.2 kcal/mol.¹¹⁰ The scarcity of accurate experimental measurements for boron-containing molecules makes it difficult to judge among the various values. In a photoionization study of BH₃ and B₂H₆, Ruscic *et al.*¹¹¹ addressed this issue and concluded that if the uncertainty in the $\Delta H_f^0(0 \text{ K}, \text{B}_2\text{H}_6)$ published by Gurvich *et al.*¹¹² was as small as reported (± 0.5 kcal/mol) their findings supported the value of Storms and Mueller. Martin and Taylor computed the atomization energies of BF and BF₃ using a composite approach based on CCSD(T).¹¹³ After using these results to analyze the heat of formation of the boron atom, they arrived at a similar conclusion. In other thermochemical work on small boron-containing molecules,^{5,114} we followed the suggestion of Ruscic *et al.*, although this is clearly an area that requires more work. In the present investigation, we shall adopt the boron heat of formation proposed by Karton and Martin,¹¹⁵ namely, $\Delta H_f^0(0 \text{ K}) = 135.1 \pm 0.2$ kcal/mol. This value is based on experimental heats of formation of BF₃ and B₂H₆ coupled with W4 calculations of their TAEs. Bauschlicher, jr. *et al.*¹¹⁶ previously recommended the same value with somewhat larger error bars of ± 0.75 kcal/mol. Results for eight boron-containing species are presented here, but the experimental uncertainty is such that only two of them (BH and B₂H₆) are included in our statistical analysis.

The experimental uncertainty for aluminum listed in the NIST-JANAF tables is also large. Consequently, we have also chosen to use the value recommended by Karton and Martin,¹¹⁵ $\Delta H_f^0(0 \text{ K}) = 80.2 \pm 0.4$ kcal/mol.

TABLE VII. Best composite theoretical and experimental heats of formation at 298.15 K (kcal/mol). [ATcT values are often reported as zero-point inclusive atomization energies. For purposes of this paper they have been converted to $\Delta H_f(298\text{ K})$ values.]

System	Theory	Expt.	System	Theory	Expt.
H ₂	0.00 ± 0.02	0.00 ^{a,b}	CH ₂ (³ B ₁)	93.4 ± 0.2	93.46 ± 0.06 ⁱ
LiH	33.2 ± 0.2	33.28 ± 0.009 ^c	CH ₂ (¹ A ₁)	102.5 ± 0.2	102.45 ± 0.38 ^o
Li ₂	51.5 ± 0.3	51.6 ± 0.7 ^{b,d}	CH ₃	35.0 ± 0.2	34.97 ± 0.03 ⁱ
HCl	-22.0 ± 0.2	-22.06 ± 0.05 ^b	CH ₄	-17.8 ± 0.2	-17.89 ± 0.03 ^f
HBr	-8.5 ± 0.2	-8.67 ± 0.4 ^e	NH	85.8 ± 0.2	85.66 ± 0.07 ⁱ
HI	6.4 ± 0.2	6.30 ± 0.05 ^b	NH ₂	44.4 ± 0.2	44.60 ± 0.05 ⁱ
ClO	24.5 ± 0.3	24.29 ± 0.2 ^b	NH ₃	-10.7 ± 0.3	-10.75 ± 0.01 ⁱ
HOCl	-18.1 ± 0.4	-18.14 ± 0.4 ^f	OH	9.0 ± 0.1	9.03 ± 0.01 ⁱ
BeH	81.0 ± 0.2	76.7 ± 7 ^b	HF	-65.3 ± 0.2	-65.16 ± 0.01 ^P
BH	106.1 ± 0.1	105.9 ± 0.6 ^g	C ₂	198.0 ± 0.3	197.94 ± 0.91 ^f
B ₂	205.6 ± 0.2	198.3 ± 8 ^b	C ₂ H	135.7 ± 0.2	135.49 ± 0.06 ⁱ
B ₂ H ₆	8.8 ± 0.6	8.75 ± 0.48 ^h	C ₂ H ₂	54.6 ± 0.3	54.42 ± 0.06 ⁱ
BN	144.9 ± 0.3	134.8 ± 14 ^h	C ₂ H ₄	12.6 ± 0.4	12.54 ± 0.07 ^b
BO	2.4 ± 0.3	0.0 ± 1.9 ^b	C ₂ H ₆	-20.2 ± 0.3	-20.17 ± 0.07 ^q
BF	-24.3 ± 0.2	-25.6 ± 2.4 ^h	C ₃ H ₆	13.0 ± 0.9	12.74 ± 0.14 ^f
BP	133.9 ± 0.2	None	C ₄ H ₆	26.3 ± 1.1	26.10 ± 0.14 ^s
BCl	43.7 ± 0.3	41.5 ± 6 ^h	HO ₂	-20.7 ± 0.3	-20.61 ± 0.15 ^f
CH	142.5 ± 0.1	142.44 ± 0.06 ⁱ	H ₂ CO	-26.1 ± 0.3	-26.13 ± 0.06 ^f
HCO	10.0 ± 0.3	9.90 ± 0.05 ⁱ	CO	26.4 ± 0.3	-26.51 ± 0.04 ⁱ
CF	-58.9 ± 0.2	-58.91 ± 0.15 ⁱ	CO ₂	-94.1 ± 0.4	-94.14 ± 0.02 ⁱ
CF ₂	-46.4 ± 0.3	-45.7 ± 0.3 ^j	H ₂ O ₂	-32.0 ± 0.3	-32.43 ± 0.02 ⁱ
CF ₃	-112.1 ± 0.4	-112.4 ± 1 ^b	FO	26.6 ± 0.2	26.58 ± 0.11 ⁱ
CN	104.0 ± 0.3	103.92 ± 0.06 ⁱ	FOO	5.8 ± 0.3	6.07 ± 0.5 ^b
C ₂ N ₂	74.1 ± 0.6	73.87 ± 0.43 ^b	PH ₃	1.2 ± 0.3	1.29 ± 0.41 ^b
CS	67.0 ± 0.3	67.0 ± 6 ^b	P ₂	34.5 ± 0.4	34.33 ± 0.5 ^b
CS ₂	27.8 ± 0.4	27.95 ± 0.2 ^b	S ₂	29.6 ± 0.3	30.69 ± 0.07 ^j
OCS	-34.1 ± 0.4	-33.08 ± 0.4 ^b	SO	1.0 ± 0.3	1.20 ± 0.3 ^b
NO	21.9 ± 0.3	21.81 ± 0.02 ⁱ	SO ₂	-71.5 ± 0.6	-71.45 ± 0.05 ^k
HNO	25.6 ± 0.3	25.57 ± 0.03 ⁱ	SO ₃	-94.7 ± 0.8	-94.59 ± 0.17 ^b
N ₂	0.2 ± 0.3	0.12 ± 0.007 ⁱ	ClF	-13.2 ± 0.3	-13.31 ± 0.07 ^t
NF	55.7 ± 0.3	55.7 ± 0.7 ^j	BrO	29.6 ± 0.3	29.5 ± 0.1 ^u
NF ₂	7.9 ± 0.3	8.23 ± 1.2 ^j	BrF	-13.8 ± 0.3	-13.97 ± 0.41 ^b
NF ₃	-31.3 ± 0.7	-31.5 ± 0.2 ^j	BrCl	3.4 ± 0.3	3.45 ± 0.01 ^v
NP	43.0 ± 0.4	41.0 ± 3.6 ^h	Cl ₂	<0.1 ± 0.3	0.0 ± 0.003 ^w
N ₂ O	19.9 ± 0.4	19.84 ± 0.03 ^f	Br ₂	7.4 ± 0.3	7.39 ± 0.03 ^b
NO ₂	8.2 ± 0.3	8.14 ± 0.02 ^f	SiO	-22.3 ± 0.3	-24.0 ± 2 ^b
O ₂	0.0 ± 0.2	0.00 ± 0.00 ⁱ	HS	33.7 ± 0.2	33.56 ± 0.8 ^h
O ₃	33.9 ± 0.4	33.82 ± 0.01 ^k	H ₂ S	-5.3 ± 0.2	-5.33 ± 0.07 ^f
F ₂	0.0 ± 0.2	0.00 ± 0.03 ⁱ	Si ₂	140.5 ± 0.3	141.0 ± 3.1 ^b
F ₂ O	5.9 ± 0.3	5.86 ± 0.48 ^j	HO ₂	3.0 ± 0.2	2.91 ± 0.05 ⁱ
H ₂ O	-57.8 ± 0.2	-57.83 ± 0.01 ⁱ	CH ₃ O	5.5 ± 0.3	5.02 ± 0.50 ^o
					5.28 ± 0.33 ^x
ClCN	32.9 ± 0.5	32.97 ^b	CH ₃ OH	-48.0 ± 0.6	-48.04 ± 0.14 ^h
HONO	-18.8 ± 0.7	-18.85 ± 0.14 ^j	CH ₃ CO	-2.3 ± 0.8	-2.46 ± 0.43 ^o
Al ₂	127.6 ± 0.2	125.63 ± 1.4 ^l	C ₃ H ₈	-25.3 ± 0.9	-25.02 ± 0.12 ^f
PO	-7.1 ± 0.4	-7.07 ± 1.0 ^j	PS	38.1 ± 0.3	36.0 ± 2.9 ^b
FS	1.2 ± 0.2	3.1 ± 1.5 ^b	C ₂ H ₄ O ox.	-12.5 ± 0.9	-12.58 ± 0.15 ^b
CF ₂ O	-145.1 ± 0.5	-149.1 + 1/4 / -0.7 ^m	C ₂ H ₄ O ac.	-39.8 ± 0.8	-39.70 ± 0.12 ^f
CH ₂ F ₂	-108.0 ± 0.3	-108.20 ± 0.24 ⁱ	C ₂ H ₂ O	-11.6 ± 0.8	-11.40 ± 0.40 ^s
SiS	28.0 ± 0.2	25.3 ± 3 ^b	CH ₃ Cl	-19.8 ± 0.4	-19.57 ± 0.14 ^j

TABLE VII. (Continued.)

System	Theory	Expt.	System	Theory	Expt.
N ₂ H ₂	48.1 ± 0.4	50.64 ± 2.4 ^h	HCN	30.9 ± 0.3	30.93 ± 0.04 ⁱ
N ₂ H ₄	23.0 ± 0.6	22.75 ± 0.12 ^j	H ₂ SiO	-24.5 ± 0.4	None
CH ₂ Cl ₂	-22.0 ± 0.5	-22.80 ± 0.18 ^j	SiH	70.48 ± 0.2	90.0 ± 1.9 ^b
K ₂	29.6 ± 0.1	29.57 ± 0.004 ⁿ	I ₂	15.1 ± 0.4	14.92 ± 0.02 ^b
KF	-78.2 ± 0.3	-78.1 ± 0.5			

^aNIST-JANAF reports $D_0=103.267 \pm 0.003$ kcal/mol, compared to the present theoretical value of 103.27 ± 0.02 kcal/mol. The $\Delta H_f(298\text{ K})$ of Li has an uncertainty of 0.24 kcal/mol.

^bReference 105.

^cReference 138.

^dNIST-JANAF reports $D_0=23.86 \pm 0.02$ kcal/mol, compared to the present theoretical value of 23.99 ± 0.3 kcal/mol.

^eReference 106.

^fReference 139.

^gReference 141.

^hReference 112.

ⁱATcT.

^jReference 124.

^kReference 144.

^lReference 148.

^mReference 149.

ⁿReference 131.

^oReference 122.

^pReference 140.

^qATcT-Karton (Ref. 88).

^rReference 142.

^sReference 143.

^tReference 78.

^uReference 145.

^vReference 146.

^wReference 147.

^xReference 123.

Silicon is another element whose heat of formation is not well established. NIST-JANAF lists $\Delta H_f^0(0\text{ K, si}) = 106.6 \pm 1.9$ kcal/mol,¹⁰⁵ while the CODATA tables contain a slightly smaller value, at 106.5 ± 1.9 kcal/mol.¹⁰⁶ For the present work, we have chosen to use a value of 107.4 ± 0.6 kcal/mol, as recommended by Feller and Dixon⁷ in a study of small silicon-containing molecules. This value is in excellent agreement with the 107.2 ± 0.2 kcal/mol value of Karton and Martin,¹¹⁵ which was derived from W4 calculations on SiH₄, Si₂H₆, and SiF₄ in a similar fashion to their B atom heat of formation.

Although not in the same category as boron, aluminum, and silicon, the $\Delta H_f^0(0\text{ K})$ for phosphorus is less well established than the other first and second row elements. The NIST-JANAF tables give a value of 75.42 ± 0.24 kcal/mol and the CODATA tables list 75.45 ± 0.24 kcal/mol. Karton and Martin explored this issue in a study of P₂ and P₄.⁹⁵ Their best estimate for $\Delta H_f^0(0\text{ K, P})$, 75.54 ± 0.1 kcal/mol, is within the error bars of the NIST-JANAF and CODATA compilations. In this study we have adopted the NIST-JANAF tables.

Iodine is the heaviest element considered in this study. Not surprisingly, diatomic I₂ (¹Σ_g⁺) required special attention. In an earlier study of I₂, we incorporated a second order SO correction of 2.05 kcal/mol obtained with MOLPRO into our results.⁹ First, the lowest SO coupled eigenstates were obtained by diagonalizing relatively small SO matrices in a basis of pure spin (Λ -S) eigenstates. In each case, the identity of the electronic states used as an expansion basis was

restricted to all states (singlets and triplets) that correlated in the dissociation limit to the ground state atomic products (six singlets and six triplets). Basis sets of augmented triple-zeta quality were employed, and the electronic states and SO matrix elements were obtained in singles-only multireference CI calculations with a full valence CAS reference function. The same procedure produced excellent results for the corresponding third row system, Br₂. A newer and more sophisticated treatment of this effect by Shepler *et al.*⁷⁹ yielded a second order correction of 1.63 kcal/mol, which we have adopted in the current study.

Weigend and Ahlrichs¹¹⁷ noted the importance of extra tight *f* functions for polarizing the inner *d* orbitals in main group elements from the fourth and fifth rows of the Periodic Table. This phenomenon is reminiscent of the much-discussed need for tight *d* functions at the HF level in second row elements Al–Ar.^{51,118} For testing purposes, we extended the iodine basis sets to the aug-cc-pV6Z-PP level and optimized a single set of *f* functions for I₂ at the HF level. The impact on the CCSD(T)(FC) dissociation energy and bond length is shown in Fig. 4. In the absence of the tight *f* functions, the aug-cc-pVn.Z-PP ($n=2-5$) sequence gives all appearances of smoothly approaching an apparent CBS limit while presenting no evidence of any underlying problem. Although the aug-cc-pV6Z-PP results continue to monotonically increase D_e (and decrease r_e), they display a small but unmistakable deviation from the convergence pattern estab-

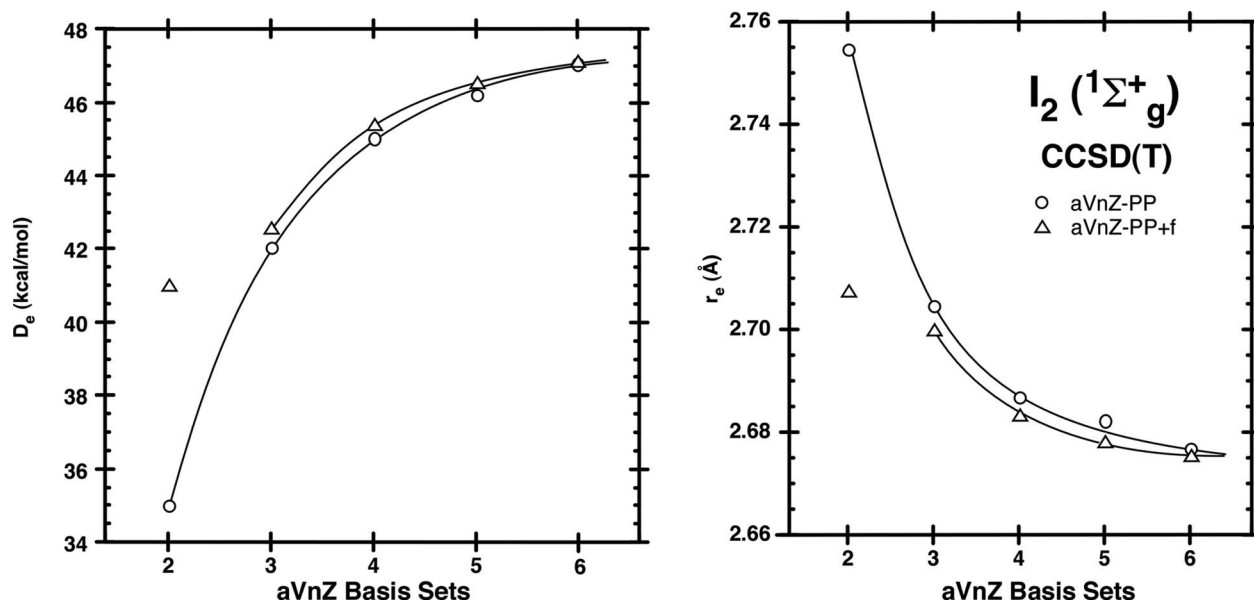


FIG. 4. Impact of tight f functions on the dissociation energy and bond length of I_2 .

lished by the smaller basis sets. This can be traced to the presence of a tight f function ($\zeta_f=2.5$) that is not present in the smaller DZ–5Z sets.

Unlike the situation with the second row elements, where d functions are present in even the aug-cc-pVDZ basis, there are no f functions in the aug-cc-pVDZ-PP basis. Thus, the aug-cc-pVDZ-PP+f data points in Fig. 4 are somewhat anomalous, reflecting the fact that the optimized exponent ($\zeta_f=0.3$) is too small to play the role of a “tight” function. For the TZ–5Z basis sets, the value of the initial tight f exponent ranged from 2.1 to 2.9. Because the 6Z set already contained a tight f function, the exponent of the added function increased to 8.9. In terms of magnitude, the addition of a single set of tight f functions to a fourth row element is much less important than the addition of tight d functions to second row elements. Consider Cl_2 , which is isoelectronic with I_2 . At the augmented triple-zeta level, the addition of a tight d function increases D_e by 1.2 kcal/mol and shortens r_e by 0.0102 Å, whereas the corresponding changes for I_2 are 0.4 kcal/mol and 0.0044 Å. However, the impact of a tight f set on iodine is more pronounced in a polar diatomic such as IO (${}^2\Pi$) where there is a significant change in the oxidation state between the molecule (+2) for I and the atomic asymptote. At the TZ basis set level, the addition of a tight f set increased the binding energy by almost 1 kcal/mol. Even at the 5Z level, the difference between binding energies computed with and without the tight f functions is more than 0.8 kcal/mol. Work is in progress on a more consistent way of incorporating tight f functions in a balanced manner into the correlation consistent basis set family.

An indication of the growth in the connected triples correction to the atomization energies of the normal alkanes is given in Fig. 5. Even for a system as small as butane, C_4H_{10} , this component of the HO correction approaches the definition of chemical accuracy (± 1 kcal/mol). Fortunately, as seen in Fig. 6, the overall HO correction grows much more slowly due to the opposing signs of the triples and quadruples.

We have previously reported the results of a theoretical study of the enthalpies of formation of FO (${}^2\Pi_{3/2}$), F_2O (1A_1), and FOO (${}^2A''$).¹⁰ Of the three systems, the last presented the greatest challenge, with our best estimate differing from the experimental values in NIST-JANAF [$\Delta H_f^0(298\text{ K})=6.07 \pm 0.48$ kcal/mol],¹⁰⁵ Lyman and Holland¹⁹³ [$\Delta H_f^0(298\text{ K})=5.49 \pm 0.40$ kcal/mol], and Pagsberg *et al.* [$\Delta H_f^0(298\text{ K})=6.24 \pm 0.50$ kcal/mol]¹¹⁹ by over

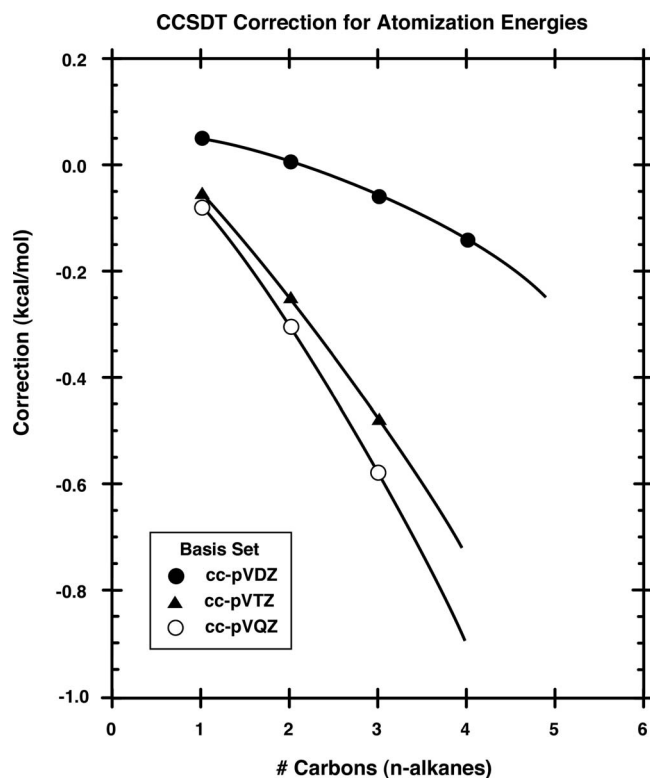


FIG. 5. Growth in the CCSDT(FC) corrections to the atomization energies of n -alkanes as a function of the number of carbon atoms and the cc- VnZ basis sets. The C_2H_6 and C_3H_8 cc-pVQZ data points were estimated by extrapolating the cc-pVDZ and cc-pVTZ energies with a $1/\ell_{\max}^3$ formula.

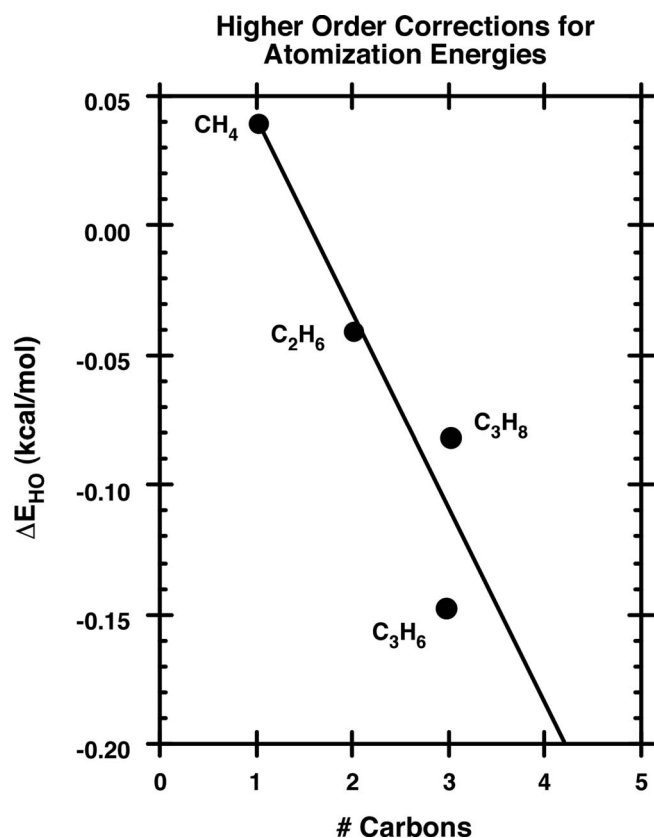


FIG. 6. Growth of the total HO correction to the atomization energy for alkanes.

3 kcal/mol. More recently, work by Denis and Ventura¹²⁰ emphasized the problems arising from spin contamination at the UCCSD(T) level of theory. They concluded that CCSDT improves agreement with experiment, whereas we find at the RCCSDT(FC)/cc-pVQZ level of theory that the effects of the iterative triples is very small (-0.02 kcal/mol) and is completely swamped by the contribution from quadruples.

The methoxyl radical, CH₃O (X^2E), presents some unusual challenges because the potential energy surface is characterized by a Jahn–Teller double cone. Our calculations were performed at one of the three symmetry-equivalent $^2A'$ lowest energy minima. The anharmonic ZPE was adopted from the equations-of-motion CCSD/aug-cc-pCVTZ calculations of Marenich and Boggs.¹²¹ Although we have chosen to compare our best estimate against the preferred heat of formation recently reported by Ruscic *et al.*,¹²² $\Delta H_f(298\text{ K}) = 5.02 \pm 0.5$ kcal/mol, the error with respect to the reinterpreted value¹²² originally due to Osborn *et al.*,¹²³ $\Delta H_f(298\text{ K}) = 5.28 \pm 0.3$ kcal/mol, is only half as large. The best value obtained from the current work is in close agreement with the recommended value, 5.6 ± 0.2 kcal/mol, of Marenich and Boggs,¹²¹ which was based on an average of four enthalpies of reaction.

Of the 107 molecules selected for this study, 91 possess an associated experimental uncertainty of ± 1 kcal/mol or less. For this group, we find $\epsilon_{\text{MAD}} = 0.15$ kcal/mol ($\epsilon_{\text{rms}} = 0.24$ kcal/mol) at the best level of theory. The only species exceeding chemical accuracy is S_2 ($^3\Sigma_g^-$), with an error of 1.05 kcal/mol. The entire CRDB contains an additional eight

molecules treated with the same general procedure as outlined here and with similar experimental uncertainties but lacking the HO correction. The agreement with experiment for this slightly larger set is $\epsilon_{\text{MAD}} = 0.19$ kcal/mol, but that may be due to partial cancellation of error. As demonstrated previously,^{2,19} even without the numerous smaller corrections described here, the CCSD(T)(FC) method by itself exhibits monotonically improving agreement with experimental atomization energies as the quality of the basis set is improved from aug-cc-pVDZ ($\epsilon_{\text{MAD}} = 35.4$ kcal/mol) to aug-cc-pV7Z ($\epsilon_{\text{MAD}} = 1.3$ kcal/mol). This trend relies in part on a cancellation of error. Driving the error even lower requires the introduction of the more computationally intensive components that are the primary topic of this paper.

If we further restrict our attention to the still smaller subset of molecules with experimental uncertainties of ± 0.15 kcal/mol or less, there are 49 examples and $\epsilon_{\text{MAD}} = 0.10$ kcal/mol ($\epsilon_{\text{rms}} = 0.18$ kcal/mol). A notable exception among this group is S_2 , for which the Burcat and Ruscic,¹²⁴ NIST-JANAF,¹⁰⁵ and CODATA (Ref. 106) compilations all list $\Delta H_f(298\text{ K}) = 30.69 \pm 0.07$ kcal/mol, compared to the best theoretical estimate of 29.77 ± 0.3 kcal/mol. The present result is consistent with the recent D_0 values (101.4 and 101.66 kcal/mol) reported by Peterson *et al.*¹²⁵ With a T_1 value of 0.009, there is little evidence to suggest a potential problem for coupled cluster theory. Given the high level of agreement for the other systems, it suggests that there may be a problem with the experimental heat of formation. This position is supported by recent theoretical work on 35 sulfur-containing molecules by Denis.⁶³ We note that the heat of formation of S_2 was measured from the equilibrium for H₂S with H₂ and S_2 , as well as from measurements of S_2 over elemental sulfur. The experimental dissociation energy measured spectroscopically of 100.69 kcal/mol also is too low.¹²⁶ If S_2 is dropped from the list, the ϵ_{MAD} for the remaining 48 species is 0.08 kcal/mol ($\epsilon_{\text{rms}} = 0.10$ kcal/mol). The same collection of molecules possesses an average experimental uncertainty of 0.06 kcal/mol, suggesting that the current level of theory, on average, is of similar accuracy.

We now discuss the two approaches for assigning uncertainty to theoretical predictions discussed previously. The first approach adopts a statistical measure of accuracy based on the performance of the model for a presumed accurate reference set. The second approach relies on a molecule-by-molecule error analysis of each of the major components contributing to the property of interest. For the group of 48 molecules with experimental uncertainties of ± 0.15 kcal/mol or less, the average theoretical uncertainty based on the second approach (see Tables VI and VII) is 0.29 kcal/mol, whereas the MAD measure is only one-third of that. Consequently, it appears that the second approach produces conservative uncertainty estimates roughly equivalent to twice the rms error and more in line with a 95% confidence value. The fact that both approaches deliver similar measures of uncertainty for this collection of small molecules is reassuring, although it may not always be the case.

The admittedly crude measure of uncertainty in the CCSD(T)(FC) basis set limit adopted here (half the spread in the CBS estimates) grows rapidly with the size of the system,

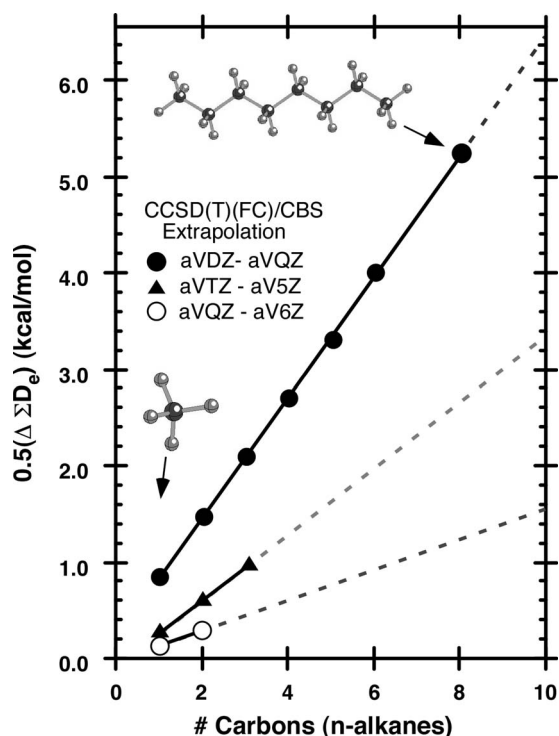


FIG. 7. Growth in the uncertainty of the CCSD(T)(FC) CBS limit atomization energy of alkanes as measured by half the spread in the CBS extrapolations.

as shown in Fig. 7, where half the spread in the CBS extrapolations is plotted as a function of both the number of carbon atoms in an alkane chain and as a function of the quality of the basis sets. It appears that for a system the size of *n*-octane, one might need a basis set of aug-cc-pV6Z quality in order to ensure ± 1 kcal/mol accuracy based on this metric. Although it is currently impossible to perform a calculation with 3798 basis functions, *n*-pentane, *n*-hexane, and *n*-octane have all been treated with the same CCSD(T) approach using a smaller basis set (up to aug-cc-pVQZ) with excellent results, which provides us with some assurance that well-crafted approaches that rely on partial cancellation of error can be very effective.¹² Moreover, the development of new explicitly correlated methods may make calculations comparable to CCSD(T)/aug-cc-pV6Z on octane a possibility in the near future.

B. Molecular structures

Whereas the chemical literature contains many high accuracy thermochemical studies, the corresponding number of reports devoted to accurate molecular structure determinations is smaller, especially for polyatomics. Large basis set coupled cluster geometry optimizations of polyatomic molecules are expensive due in part to current software limitations. Early results from Rucharski *et al.* indicated that HO corrections [i.e., beyond CCSD(T)] to bond lengths induced changes on the order of 0.001–0.002 Å.¹²⁷ Ruden *et al.*⁸² examined the effects of connected quadruple and quintuple excitations on the bond lengths and harmonic frequencies of four first row diatomics. The largest quadruple correction (F_2) was 0.0043 Å. The present study is closer to the work of

Heckert *et al.*,¹²⁸ who used a combination of large basis set CCSD(T)(FC), plus CV, CCSDT, and CCSDTQ corrections to determine the structures of 12 small closed shell and 5 open shell species. They reported a standard deviation with respect to experimental bond lengths of 0.000 36 Å. A subsequent paper by Heckert *et al.*⁷⁰ dealing with the same collection of molecules examined the effect of incorporating an extrapolation to the CBS limit. Basis sets as large as cc-pV6Z were used. However, while basis set extrapolation was found to be effective in reducing the basis set truncation error, extrapolation alone was insufficient to improve agreement with experiment. In fact, the use of CBS extrapolation caused the level of agreement to deteriorate slightly. Only by including relativistic corrections and pentuple excitations was improvement seen.

Here we follow the broad outline of the procedure described in earlier work^{1,2,67} which differs somewhat from the approach of Heckert *et al.*,¹²⁸ who were able to exploit analytical coupled cluster gradient techniques. Consistent with the approach for computing atomization energies, we used the aug-cc-pVnZ basis set sequence which includes additional diffuse functions, whereas Heckert *et al.* used the regular cc-pVnZ sets. For general polyatomic species, the internal coordinates were directly extrapolated to the CBS limit via a simple exponential function. Heckert *et al.* used an exponential for the SCF component and $1/\ell_{\max}^3$ for the CCSD(T) correlation component. In our work, the CV correction was also extrapolated to the CBS limit, although this extrapolation typically results in only small changes in the structural parameters. CCSDTQ5 or FCI corrections to the structures were only possible for a few of the molecules in this study. As noted by Valeev and Sherrill,⁹⁰ the DBOC can be unexpectedly large for some light systems, such as BH ($^1\Sigma^+$), where it increased the bond length by 0.0007 Å. DBOCs obtained from CISD/aug-cc-pVTZ calculations were included for some first row hydrides and CH_4 .

A comparison of the best level of theory, shown in Table VIII, with experiment yielded MADs of 0.0027 Å (AH bond lengths, 49 comparisons), 0.0010 Å (AB bond lengths, 79 comparisons), and 0.2° (bond angles, 30 comparisons). These statistics were based on a subset of the molecules possessing accurate experimental structures. Most polyatomic molecules with four or more atoms were excluded because of their relatively large error bars. For example, the microwave structure of propane reported by Lide Jr.,¹²⁹ included uncertainties of ± 0.002 Å (r_{CC}), ± 0.002 (r_{CH} , CH_2 group), and ± 0.010 Å (r_{CH} , CH_3 group). Polyatomic species with semiexperimental structures were included.

In general, the level of agreement between theory and experiment for diatomics is excellent. An exception is K_2 ($^1\Sigma_g^+$), where FC CCSD(T) predicts a bond length that is 0.25 Å longer than the experimental value (3.924 33 Å) reported by Heinze *et al.*¹³⁰ and Amiot.¹³¹ Note that the older Huber and Herzberg value is still shorter, at $r_e=3.9051$ Å.⁷⁸ By expanding the active space to include the potassium $3s^2 3p^6$ electrons, CCSD(T)(CV) calculations shrink the bond length to 3.9305 Å at the basis set limit. The CV SR correction further shrinks the bond, while HO correlation lengthens it, setting up a tug of war reminiscent of the situation with

TABLE VIII. Best composite theoretical and experimental molecular structures (\AA and degrees) (for B_2H_6 , x indicates the center of the molecule).

System	Theory	Expt.	System	Theory	Expt.
H_2	$r_e=0.741\ 44$	$0.741\ 44^a$	BN	$r_e=1.325\ 5$	$1.329\ r_0^w$
LiH	$r_e=1.595\ 7$	$1.595\ 7^a$	BO	$r_e=1.204\ 7$	$1.204\ 5^a$
Li_2	$r_e=2.673\ 3$	$2.672\ 9^a$	BF	$r_e=1.263\ 0$	$1.262\ 5^a$
HCl	$r_e=1.274\ 4$	$1.274\ 6^a$	BP	$r_e=1.743\ 2$	
HBr	$r_e=1.413\ 9$	$1.414\ 4^a$	BCl	$r_e=1.715\ 5$	$1.715\ 9^c$
HI	$r_e=1.609\ 6$	$1.609\ 2^a$	CH	$r_e=1.117\ 9$	$1.119\ 9^a$
ClO	$r_e=1.568\ 5$	$1.568\ 9^b$	$\text{CH}_2\ (^3B_1)$	$r_{\text{CH}}=1.075\ 5$	$1.074\ 8^x$
				$\angle = 133.9$	133.8
HOCl	$r_{\text{ClO}}=1.688\ 9$	1.690^c	$\text{CH}_2\ (^1A_1)$	$r_{\text{CH}}=1.106\ 2$	1.107^y
	$r_{\text{OH}}=0.963\ 9$	0.975^d		$\angle = 102.3$	102.4
	$\angle = 102.9$	102.5			
BeH	$r_e=1.341\ 4$	$1.342\ 6^a$	CH_3	$r_{\text{CH}}=1.076\ 1$	1.079^n
BH	$r_e=1.230\ 1$	$1.232\ 2^c$	CH_4	$r_{\text{CH}}=1.086\ 1$	$1.087\ 0^z$
B_2	$r_e=1.589\ 9$	$1.590\ 0^a$	NH	$r_e=1.036\ 0$	$1.036\ 2^a$
B_2H_6	$r_{\text{BX}}=0.875\ 0$	$0.881\ 5^f$	NH_2	$r_{\text{NH}}=1.024\ 0$	1.024^n
	$r_{\text{BH}}=1.183\ 7$	$1.201\ 0$		$\angle = 103.0$	103
	$\angle_{\text{XBH}}=118.9$	119.5			
	$r_{\text{XH}}=0.972\ 8$	$0.982\ 5$			
NH_3	$r_{\text{NH}}=1.011\ 2$	$1.011\ 6^a$	HOF	$r_{\text{OF}}=1.434\ 9$	$1.435\ 0^{aa}$
	$\angle_{\text{HNH}}=106.8$	106.7		$r_{\text{OH}}=0.966\ 8$	0.9657
OH	$r_e=0.969\ 7$	$0.969\ 7^a$		$\angle_{\text{HOF}}=97.8$	97.5
HF	$r_e=0.916\ 8$	$0.916\ 8^a$	HCO	$r_{\text{CO}}=1.175\ 8$	1.175^{ab}
				$r_{\text{CH}}=1.165\ 8$	1.125
				$\angle_{\text{HCO}}=124.4$	124.9
			H_2CO	$r_{\text{CO}}=1.203\ 8$	$1.203\ 3^{ac}$
				$r_{\text{CH}}=1.100\ 3$	$1.100\ 4$
				$\angle_{\text{HCO}}=121.7$	121.7
C_2	$r_e=1.242\ 6$	$1.242\ 5^a$	CO	$r_e=1.128\ 4$	$1.128\ 3^a$
C_2H	$r_{\text{CC}}=1.207\ 7$		CO_2	$r_{\text{CO}}=1.160\ 0$	$1.160\ 0^{ad}$
	$r_{\text{CH}}=1.062\ 6$				
C_2H_2	$r_{\text{CC}}=1.203\ 0$	$1.202\ 4^h$	CF	$r_e=1.272\ 0$	$1.271\ 8^{ad}$
	$r_{\text{CH}}=1.061\ 5$	$1.062\ 5$			
C_2H_4	$r_{\text{CC}}=1.330\ 8$	$1.330\ 5^i$	CF_2	$r_{\text{CF}}=1.297\ 6$	$1.303\ 5^{ac}$
	$r_{\text{CH}}=1.080\ 3$	$1.089\ 5$		$\angle_{\text{FCF}}=104.8$	104.8
	$\angle_{\text{CCH}}=121.4$	121.5			
C_2H_6	$r_{\text{CC}}=1.522\ 6$	1.522^j	CF_3	$r_{\text{CF}}=1.311\ 4$	1.318^o
	$r_{\text{CH}}=1.089\ 11$	1.089		$\angle_{\text{XCF}}=107.6$	108.2
	$\angle_{\text{CCH}}=111.2$	111.2			
C_3H_6	$r_{\text{CX}}=0.867\ 2$	$0.867\ 8^k$	CN	$r_e=1.172\ 1$	$1.171\ 8^{ad}$
	$r_{\text{CH}}=1.079\ 1$	$1.078\ 6$			
	$\angle_{\text{XCH}}=122.6$	122.5			
C_4H_6	$r_{\text{CC}}=1.338\ 9$	$1.337\ 6^i$	C_2N_2	$r_{\text{CC}}=1.383\ 9$	$1.383\ 9^f$
	$r_{\text{CC}}=1.454\ 9$	$1.453\ 9$		$r_{\text{CN}}=1.158\ 1$	$1.157\ 8$
	$r_{\text{CH}}=1.082\ 5$	$1.081\ 9$			
	$r_{\text{CH}}=1.079\ 9$	$1.079\ 3$			
	$r_{\text{CH}}=1.084\ 8$	$1.084\ 7$			
	$\angle_{\text{CCC}}=123.6$	122.6			
CS_2	$r_{\text{CS}}=1.553\ 1$	1.553^l	CS	$r_e=1.535\ 0$	$1.534\ 9^{ad}$
OCS	$r_{\text{CS}}=1.561\ 7$	1.561^j	F_2	$r_e=1.412\ 2$	$1.411\ 9^a$
	$r_{\text{CO}}=1.156\ 3$	1.157			
NO	$r_e=1.150\ 8$	$1.150\ 8^a$	F_2O	$r_{\text{FO}}=1.405\ 0$	$1.405\ 3^{ag}$
				$\angle_{\text{FOF}}=103.0$	103.1
HNO	$r_{\text{NO}}=1.208\ 3$	$1.208\ 7^m$	H_2O	$r_{\text{OH}}=0.957\ 6$	$0.957\ 2^{ah}$
	$r_{\text{NH}}=1.051\ 9$	$1.053\ 6$		$\angle_{\text{HOH}}=104.5$	104.5
	$\angle_{\text{HNO}}=108.2$	108.1			
			H_2O_2	$r_{\text{OO}}=1.451\ 0$	$1.455\ 6^{ai}$
				$r_{\text{OH}}=0.962\ 7$	0.967
				$\angle_{\text{OOH}}=100.0$	102.3
				$\angle_d=112.9$	119.1
N_2	$r_e=1.097\ 6$	$1.097\ 7^a$	FO	$r_e=1.354\ 1$	$1.354\ 1^a$

TABLE VIII. (Continued.)

System	Theory	Expt.	System	Theory	Expt.
NF	$r_e=1.317\ 2$	1.319 9 ^a	FOO	$r_{OO}=1.192\ 4$ $r_{FO}=1.657\ 9$ $\angle_{OOH}=110.9$	1.200 ^u 1.649 111.2
			PH ₃	$r_{PH}=1.411\ 6$ $\angle_{HPH}=93.4$	1.421 ^s 93.3
NF ₂	$r_{NF}=1.346\ 3$ $\angle_{FNF}=103.2$	1.370 ^s 104.2	P ₂	$r_e=1.893\ 5$	1.893 4 ^a
NF ₃	$r_{NF}=1.364\ 9$ $\angle_{FNF}=102.1$	1.365 ^o 102.4	S ₂	$r_e=1.889\ 4$	1.889 2 ^a
NP	$r_e=1.491\ 2$	1.490 9 ^a	SO	$r_e=1.481\ 4$	1.481 1 ^a
N ₂ O	$r_{NN}=1.126\ 5$ $r_{NO}=1.185\ 5$	1.127 3 ^p 1.185 1	SO ₂	$r_{SO}=1.432\ 2$ $\angle_{OSO}=119.3$	1.432 1 ^{ak} 119.5
NO ₂	$r_{NO}=1.194\ 4$ $\angle_{ONO}=133.9$	1.194 6 ^q 133.9	SO ₃	$r_{SO}=1.418\ 8$	1.417 3 ^{ak}
O ₂	$r_e=1.207\ 7$ $R_{OO}=1.272\ 4$ $\angle_{OOO}=116.9$	1.207 5 ^a 1.271 7 ^t 116.8	ClF	$r_e=1.628\ 0$	1.628 3 ^a
BrF	$r_e=1.757\ 5$	1.758 9 ^a	BrO	$r_e=1.716\ 6$	1.717 2 ^{al}
BrCl	$r_e=2.135\ 7$	2.136 1 ^a	FS	$r_e=1.596\ 6$	1.596 2 ^{am}
			CF ₂ O	$r_{CO}=1.700\ 0$ $r_{CF}=1.309\ 4$ $\angle_{FCO}=126.1$	1.170 ^j 1.317 126.2
Cl ₂	$r_e=1.987\ 9$	1.988 0 ^a	CH ₂ F ₂	$r_{CH}=1.086\ 8$ $r_{CF}=1.352\ 7$	1.092 ^{an} 1.358
Br ₂	$r_e=2.280\ 7$	2.281 0 ^a	SiS	$r_e=1.929\ 4$	1.929 3
SiO	$r_e=1.510\ 0$	1.509 7 ^a	N ₂ H ₂	$r_{NN}=1.245\ 3$ $r_{NH}=1.028\ 3$ $\angle_{NNH}=106.4$	1.252 ^{ao} 1.028 106.9
HS	$r_e=1.340\ 2$	1.340 4 ^a	CH ₂ Cl ₂	$r_{ClC}=1.762\ 8$ $r_{CH}=1.081\ 7$	1.772 ^f 1.091
H ₂ S	$r_{SH}=1.335\ 7$ $\angle_{HSH}=92.0$	1.328 ⁿ 92.2	CH ₃ O	$r_{CO}=1.368\ 8$ $r_{CH}=1.101\ 4$ $r_{CH}=1.092\ 7$	
Si ₂	$r_e=2.246\ 3$	2.246 ^a	CH ₃ OH	$r_{CO}=1.417\ 3$ $r_{CH}=1.085\ 7$ $r_{CH}=1.091\ 2$ $r_{OH}=0.957\ 0$	1.427 ^{ap} 1.096 1.096 0.956
HO ₂	$r_{OO}=1.329\ 8$ $r_{SH}=0.969\ 9$ $\angle_{HSH}=104.3$	1.331 ^s 0.971 104.3	CH ₃ CO	$r_{CO}=1.179\ 4$ $r_{CC}=1.507\ 7$ $r_{CH}=1.089\ 7$ $r_{CH}=1.087\ 6$	
CiCN	$r_{CN}=1.159\ 0$ $r_{ClC}=1.630\ 3$	1.161 ^o 1.629	C ₃ H ₈	$r_{CC}=1.522\ 1$ $r_{CH}=1.089\ 4$ $r_{CH}=1.090\ 8$ $r_{CH}=1.091\ 8$	1.526 ^{aq} 1.095 1.091 1.096
HONO	$r_{OH}=0.965\ 2$ $r_{NO}=1.425\ 1$ $r_{NO}=1.168\ 4$ $\angle_{ONO}=110.7$	0.964 7 ^m 1.425 0 1.168 9 110.7	PS	$r_e=1.897\ 4$	1.897 7 ^{ar}
Al ₂	$r_e=2.701\ 4$	2.701 ^t	C ₂ H ₄ O ox.	$r_{CO}=1.425\ 2$ $r_{CH}=1.082\ 0$	1.436 3 ^{as} 1.080 2
PO	$r_e=1.476\ 6$	1.476 4 ^a	C ₂ H ₄ O ac.	$r_{CC}=1.497\ 9$ $r_{CH}=1.085\ 9$ $r_{CH}=1.090\ 9$ $r_{CH}=1.105\ 3$ $r_{CO}=1.206\ 2$	1.501 ^{at} 1.086 1.086 1.114 1.216
C ₂ H ₂ O	$r_{CC}=1.312\ 6$ $r_{CO}=1.160\ 7$ $r_{CH}=1.076\ 1$	1.314 ^j 1.161 1.077	H ₂ SiO	$r_{SiO}=1.514\ 8$ $r_{SiH}=1.472\ 6$ $\angle_{HSiO}=124.0$	1.515 ^{au} 1.472 124.0

TABLE VIII. (Continued.)

System	Theory	Expt.	System	Theory	Expt.
CH ₃ Cl	$r_{\text{CCl}}=1.777\ 2$	1.781 ^f	SiH	$r_e=1.519\ 1$	1.519 7 ^a
	$r_{\text{NO}}=1.083\ 3$	1.096			
	$\angle_{\text{ClCH}}=108.4$	108.4			
HCN	$r_{\text{CN}}=1.153\ 2$	1.153 2 ^v	KF	$r_e=2.172\ 9$	2.171 6 ^w
	$r_{\text{CH}}=1.065\ 0$	1.065 0			
I ₂	$r_e=2.663\ 8$	2.666 3 ^a	K ₂	$r_e=3.914\ 8$	3.924 3 ^{aw}

^aReference 78. ^bReference 156.
^bReference 151. ^cReference 168.
^cReference 153. ^dReference 175.
^dReference 154. ^eReference 177.
^eReference 157. ^fReference 178.
^fReference 159. ^gReference 184.
^gReference 160. ^hReference 148.
^hReference 165. ⁱReference 187.
ⁱReference 68. ^jReference 190.
^jReference 167. ^kReference 150.
^kReference 69. ^lReference 152.
^lReference 169. ^mReference 155.
^mReference 172. ⁿReference 158.

^{aa}Reference 161. ^{ab}Reference 181.
^{ab}Reference 162. ^{ac}Reference 182.
^{ac}Reference 163. ^{ad}Reference 183.
^{ad}Reference 164. ^{ae}Reference 129.
^{ae}Reference 166. ^{af}Reference 185.
^{af}Reference 192. ^{ag}Reference 186.
^{ag}Reference 170. ^{ah}Reference 188.
^{ah}Reference 171. ^{ai}Reference 189.
^{ai}Reference 173. ^{aj}Reference 191.
^{aj}Reference 174. ^{ak}Reference 176.
^{ak}Reference 176. ^{al}Reference 179.
^{al}Reference 179. ^{am}Reference 180.
^{am}Reference 180. ^{aw}References 130 and 131.

atomization energies. Contributions from the eight deep core $2s^2 2p^6$ electrons were also investigated by means of a modification to the aug-cc-pwCV5Z basis set. The (s, p) portion of the basis set was uncontracted and two shells of tight (d, f, g, h) functions were added in an even-tempered progression. Little impact was observed on D_e (0.03 kcal/mol) and ω_e (0.02 cm⁻¹), but the bond length decreased by 0.0027 Å. The best value is still 0.01 Å shorter than experiment.

As discussed in a previous section, the I₂ molecule required special attention. For the present study we increased the size of the basis set to aug-cc-pV5Z-PP, which produced a correction to the bond length of 0.0144 Å and a theoretical r_e value that was 0.005 Å longer than experiment. More sophisticated multireference calculations with the SO CI (Ref. 132) code in the COLUMBUS package¹³³ that included all singlet, triplet, and quintet states of I₂ reduced the size of the correction to 0.0100 Å, bringing theory into much better agreement with experiment. Shepler *et al.*⁷⁹ recently reported a value of $r_e=2.6643$ Å, obtained without the inclusion of HO effects.

IV. CONCLUSION

A flexible, composite theoretical procedure utilizing a hierarchy of correlation consistent one-particle basis sets and a systematic n -particle expansion based on coupled cluster theory methods has been used to predict the atomization energies and structures of over 100 small molecules. At the highest level, as represented by the findings in this work, the current scheme incorporates (up to) 13 component pieces which were determined to be significant for at least some of the systems. The development of our approach over the past decade has been driven by the desire to achieve uniformly higher accuracy for chemical systems composed of elements spanning the complete Periodic Table. Different parts of the Periodic Table present differing methodological requirements, thus making it difficult to define a single computa-

tional regimen or model chemistry that is capable of addressing every situation without including steps that are unnecessary in many cases.

The level of accuracy was found to be comparable to the best available experimental data, with ϵ_{MAD} below 0.1 kcal/mol and 0.001 Å (AB bond lengths) for particularly well-characterized systems. The corresponding rms values are 0.10 kcal/mol and 0.002 Å. In only one case (S₂) were we unable to reproduce an experimental dissociation energy with a stated uncertainty of less than ± 0.1 kcal/mol.

The power of the approach is such that even molecules with moderate multiconfigurational character, e.g., C₂, FOO, and O₃, are well described. On the negative side, the computational cost is very high, effectively limiting the size of the chemical systems that can be addressed. Consequently, even though the number of molecules in the current collection is relatively large for this level of study, it remains much smaller than the thermochemical test sets used for less expensive methods, e.g., the G3/05 set with 270 enthalpies of formation¹³⁴ or the 600 member test set of Cioslowski *et al.*¹³⁵ As computer hardware and software continue to evolve, this situation is likely to slowly change.

In addition to the computational cost, the other difficulty shared by our approach and the similar approaches developed by other groups around the world is the problem of minimizing the uncertainties resulting from combining components of differing sign. It places a premium on careful attention to detail as we continue to probe the very limits of our capability to model molecular behavior.

While the focus of the present work has been on establishing the highest level of accuracy achievable under the constraints of our present hardware and software, we do not mean to imply that calculations of this quality are a prerequisite for obtaining accurate atomization energies and structures. Less expensive but *still balanced* combinations of components are necessary if the approach is to be applied to larger systems. A follow-up study of the typical accuracy that

can be expected from less computationally expensive approaches is in progress.

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