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A Theoretical Determination of the Heats of Formation of Furan, Tetrahydrofuran, THF-2-yl, and THF-3-yl

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Large basis set coupled cluster calculations, with corrections for core/valence, atomic spin−orbit, and scalar relativistic effects, have been used to determine the atomization energies of furan ($^1A_1$, C_4H_4O), tetrahydrofuran (^1A, C_4H_8O), and the THF-2-yl (^2A, C_4H_8O) and THF-3-yl (^2A, C_4H_8O) radicals. For furan and tetrahydrofuran, where gas-phase experimental data is available, the level of agreement between experiment and theory is very good. The 0 K heats of formation (kcal/mol) for the four systems are ΔH_f(furan) = −4.6 ± 0.5 (calcd) vs −5.2 ± 0.2 (exptl), ΔH_f(tetrahydrofuran) = −37.6 ± 0.7 (calcd) vs −37.6 ± 0.2 (exptl), ΔH_f(THF-2-yl) = 5.1 ± 1.0 (calcd), and ΔH_f(THF-3-yl) = 8.9 ± 1.0 (calcd). At 298 K the comparable values are ΔH_f(furan) = −7.7 ± 0.5 (calcd) vs −8.3 ± 0.2 (exptl), ΔH_f(tetrahydrofuran) = −44.0 ± 0.5 (calcd) vs −44.0 ± 0.2 (exptl), ΔH_f(THF-2-yl) = −0.5 ± 1.0 (calcd) and ΔH_f(THF-3-yl) = 3.6 ± 1.0 (calcd). The principal limitation on the accuracy of the composite coupled cluster approach followed in this work is the high cost of large basis set calculations on chemical systems that lack exploitable elements of symmetry. Three parametrized methods, G2, G3, and CBS-Q, were also found to be in good agreement with experiment.

Introduction

The free radical reactivity of tetrahydrofuran (THF) is of interest as a prototype for the reactivity of cyclic ethers of biological importance in radical-induced oxidation reactions. The most important of this class of cyclic ethers are the ribose and deoxyribose substructures of nucleotides, for which the formation of carbon-centered radicals and subsequent reaction with oxygen provides a key mechanism for strand breakage in DNA.[1] The accurate measurement of bond dissociation enthalpies (BDEs), heats of formation, and solvation properties is essential for the prediction of reactivity and selectivity in the oxidative free radical chemistry of cyclic ethers. Ribose is an example of a cyclic ether substructure that may possess a variety of reactive CH bonds. Experimental measurement of BDEs remains a formidable challenge for complex molecules. Many bond strengths have been reported for organic and organometallic free radicals, and relative bond dissociation enthalpies for organic structures are reliable to within 1−2 kcal/mol using a variety of gas-phase methods[2] and solution phase thermochemical cycle methods.[3] A growing number of experimental heats of formation are becoming available with absolute errors assessed to be less than 2 kcal/mol.[4,2]

Several studies of the α-CH bond in THF have been reported. An early value of $\Delta H_{f,298}$(THF-2-yl) = −4.1, corresponds to an α-CH BDE of 92 kcal/mol.[5] A more recent study[6] reports the α-CH BDE of THF to be 93.2 kcal/mol, but uses a reference value of cyclohexane of 95.5 kcal/mol. Correction of the reference to a more recent value for cyclohexane, 98.6 ± 0.4 kcal/mol,[2] yields a BDE corresponding to the formation of THF-2-yl of 96.3 kcal/mol. Finally, Laarhoven and Mulder[7] used photoacoustic calorimetry (PAC) to arrive at a gas-phase value of 92.1 ± 1.6 kcal/mol. Thus, α-CH BDE estimates span a range in energies between 92 and 96 kcal/mol.

While the recent PAC value may be the most accurate of the three determinations to date, the cited error range, ±1.6 kcal/mol, seems overly optimistic.[8] The composite error of the PAC measurement depends on (1) the absolute error in the BDE of the standard, 1,4-cyclohexadiene (76 ± 2 kcal/mol),[9] (2) the accuracy of a group correction factor for the effects of nonpolar and polar solvents,[8] (3) the composite error of sequential measurements of foreground and background PAC signals, (4) error in estimation of the quantum yield for *tert*-butoxyl radical formation in THF, (5) error in correction of the liquid-phase PAC data to the gas phase (∼1 kcal/mol),[7] and (6) for THF and related systems, the need to correct for diminution of the detected PAC signal due to the presence of the 3-hydrogens of THF.[7]

The photoacoustic method of Laarhoven, Mulder, and Wayner[8] relates a solution value heat of deposition for the reaction of *tert*-butoxyl radical with hydrogen donors to the gas-phase value of the BDE of 1,4-cyclohexadiene, 76 kcal/mol,[9] yielding gas-phase BDEs of hydrogen donors. The method requires the application of empirical corrections for each solvent category to correct between *observed* heat deposition and *predicted* heat deposition from the reaction of 1,4-cyclohexadiene and *tert*-butoxyl radical. The resulting gas-phase values can be used to obtain solution phase BDEs by correction for the enthalpy of solvation of the hydrogen atom in the solvent, 2 ± 0.5 kcal/mol.[10,11] The experimental error in PAC BDEs is estimated by Laarhoven et al. to be about 2 kcal/mol.[8] Thus, for purposes of comparison to the results in the present study, the gas-phase value of the BDE of THF to give the THF-2-yl radical, 92.1

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kcal/mol, leads to $\Delta H_{f,298}$(THF-2-yl) = −4.0± ca. 2 kcal/mol. For the THF-3-yl radical, it is assumed that the 3-H will have the BDE of cyclopentane, 97.6 kcal/mol, then $\Delta H_{f,298}$(THF-3-yl) = 1.5 ± ca. 2 kcal/mol.[12] The PAC BDE value for THF-2-yl radical thus appears to be slightly lower than expected relative to the THF-3-yl radical ($\Delta\Delta H_{f,298}$ (2→3) = 5.6 kcal/mol). All *relative* high level theoretical enthalpy differences, expected to be very reliable, between the two radicals are found to be between 4.1 and 4.8 kcal/mol. These considerations suggest that the BDE for formation of THF-2-yl does not lie below about 93 kcal/mol, and may be as high as 94 kcal/mol, depending on the BDE selected for the 3-H of THF, and error in the reference compound, 1,4-cyclohexadiene.

Error margins associated with the PAC technique and other measurements underscore the difficulties in obtaining accurate BDEs and the importance of developing theoretical methods that will reliably provide heats of formation and bond dissociation enthalpies of high accuracy, particularly for complex molecules for which the determination of radical heats of formation may be very difficult. In this study we use ab initio methods to determine the heats of formation of THF-2-yl (^{2}A, C_4H_7O) and THF-3-yl (^{2}A, C_4H_7O), two organic radicals for which experimental data is either unavailable or of questionable accuracy. To calibrate the theoretical procedure which will be used we have also examined two related organic compounds, furan ($^1A_1$, C_4H_4O) and THF (^{1}A, C_4H_8O), where reliable experimental heats of formation are available.

The past decade has seen the development of new theoretical procedures (or “model chemistries”) intended for the accurate prediction of thermochemical properties, such as heats of formation, electron affinities, and ionization potentials. These procedures can be roughly divided into two broad categories, characterized by the presence or absence of empirically adjusted parameters designed to simultaneously optimize the performance of the model for a particular training set of molecules and minimize the cost. Representative of the first category are the popular Gaussian-2 (G2)[13] and Gaussian-3 (G3)[14] methods, the bond additivity (BAC-MP4) method of Melius,[15,16] the parametrized configuration interaction (PCI-X) method,[17,18] the complete basis set (CBS) family of methods developed by Petersson and co-workers,[19−21] and the multicoefficient G2 and G3 variants.[22,23]

Many of these parametrized schemes are capable of predicting heats of formation for small-to-medium sized molecules that are chemically similar to molecules in their training sets with mean absolute deviations (ϵ_{MAD}) that approach “chemical accuracy” (1−2 kcal/mol). However, the maximum errors can be much larger. For example, the Environmental Molecule Sciences Laboratory (EMSL) Computational Results Database[24] currently contains information on the vibrationless atomization energies (ΣD_e) of 147 molecules. If we restrict ourselves to only those atomization energies with reliable experimental data, the G2 procedure was found to yield maximum positive and negative errors (relative to experiment) of +6.6 and −10.1 kcal/mol. The corresponding G3 values are smaller (+4.0 and −4.6 kcal/mol), but still exceed the target of chemical accuracy. For this same collection of atomization energies, the CBS-Q method produces a slightly smaller ϵ_{MAD}, although maximum errors were larger.

The second major category of thermochemical methods is characterized by an absence of embedded parameters. Despite greatly increased computational costs, the motivation behind this second group of methods is the hope that by avoiding empirically adjusted parameters chosen for a particular group of molecules it should be possible to achieve greater generality and since the approach permits a hierarchy of ab initio methods, ultimately, improved accuracy.

These two approaches to computational thermochemistry are more properly viewed as complementary, since parametrized methods can be applied to chemical systems that are too large for nonparametrized methods, while the latter can include very sophisticated electron correlation techniques, thus allowing them to handle novel compounds and arbitrary points on a potential energy surface. Sufficiently accurate results obtained from nonparametrized methods could provide an alternate source of thermochemical information, which might be used to augment the limited amount of experimental information available for developing new parametrized strategies.

Along with several other laboratories around the world,[25−29] we have been developing a composite theoretical approach that is intended to reliably predict a variety of thermodynamic quantities, such as heats of formation, without recourse to empirical parameters.[30−35,25,36] As described below, our approach begins with high-quality thermodynamic values (obtained from either experiment or theory). Missing pieces of information are obtained from ab initio electronic structure calculations. The method of choice is usually coupled cluster theory including single, double, and triple excitations, with the latter being handled in an approximate (perturbative) fashion.[37−39] This method, known conventionally as CCSD(T), is capable of recovering a large fraction of the correlation energy for molecules that can qualitatively be described by a single electronic configuration.[40,35]

In the present work, we apply our approach to the task of determining the heats of formation of furan, THF, THF-2-yl, and THF-3-yl. Our results will be compared to values obtained from three of the most widely used parametrized methods, G2,[13] G3,[14] and CBS-Q.[21] To date, our composite nonparametrized procedure has been applied to 77 molecules, yielding a mean absolute deviation of 0.7 kcal/mol and a maximum error of 4.4 kcal/mol. Very recent work on the heats of formation of 16 hydrocarbons up to the size of benzene[41] provides an illustration of the general level of agreement with experiment which this approach can provide. The errors for only two compounds (acetylene and cyclopropene) exceeded 1 kcal/mol, leading to revised recommended values of ΔH_f^0 for both.

Methods

The majority of the high-level theoretical thermochemical results in the EMSL Computational Results Database[24] were obtained from calculations performed with the diffuse function augmented correlation consistent family of basis sets, from double through quintuple zeta (aug-cc-pVDZ through aug-cc-pV5Z).[42,43] For our purposes, the crucial feature of the correlation consistent basis sets is the systematic way in which computed properties approach the CBS limit. This behavior facilitates an estimate of the remaining error due to the use of finite basis sets, as will be discussed below. Basis set incompleteness and limited correlation recovery are the dominant causes of error in most electronic structure calculations.

Although diffuse functions are typically of minor importance when computing the atomization energy of nonpolar, neutral species, we have nonetheless chosen to employ the aug-cc-pVxZ basis sets in our previous work so as to maintain a uniform approach that is capable of handing anions and highly polar molecules. Throughout this work, the original correlation consistent basis sets, which lack the extra shell of diffuse functions, will be denoted as VDZ, VTZ, and VQZ, whereas sets containing diffuse functions are labeled aVDZ, aVTZ, and aVQZ. The largest calculation in the present work, an aVQZ coupled cluster calculation on furan, involved 584 functions. For reference purposes, the next larger basis set in the correlation consistent sequence (aV5Z) would have resulted in 955 functions for furan and was beyond the capabilities of our present hardware and software. Only the spherical components of the Cartesian polarization functions were used.

All CCSD(T) energies were obtained with MOLPRO-2000[44] running on a single processor of an SGI Origin 2000 with 250 MHz R10000 processors. While it would have been desirable to use the aVDZ → aVQZ sequence of basis sets for all four molecules, the aVQZ basis set led to intractable calculations for molecules other than furan. The absence of sufficient exploitable symmetry in THF, THF-2-yl, and THF-3-yl created excessively long runtimes (>1 month) and very large memory requirements (>8 GB). Consequently, for these three molecules the CBS extrapolations were based on total energies obtained without the extra shell of diffuse functions. Although the lack of diffuse functions is expected to produce only a minor change in the final results, previous work on similar sized molecules showed that effect was not completely negligible if an accuracy of ±1 kcal/mol is the goal. Therefore, the CBS/DTQ atomization energies were adjusted so as to approximate the effects of the missing basis functions. A correction based on the difference in CBS/VTZ and CBS/aVTZ values for furan and the VTZ − aVTZ difference in binding energies for THF (1.0 kcal/mol) was applied in the three cases where aVQZ calculations were beyond our present capabilities.

For the THF-2-yl and THF-3-yl radicals, a further approximation was required with the VQZ basis set. CCSD(T)/VTZ calculations on these radicals required 6.3 days of computer time each, of which the triple excitations took 4.6 days. Assuming an n^3N^4 scaling, where n = number of occupied orbitals and N = unoccupied molecular orbitals, a CCSD(T)/VQZ calculation would have required ~80 days to complete. However, if we limit ourselves to single and double excitations, the calculation time is reduced to ~13 days, which while lengthy is still within the realm of possibility. Triple excitations contribute on the order of 2−6% of the correlation energy for molecules the size of benzene or smaller. Nevertheless, despite the relatively small fraction of the correlation energy, triple excitations are critical for achieving chemical accuracy. CCSD (i.e., without the triples) does very poorly at predicting atomization energies, with a mean absolute deviation that exceeds 6 kcal/mol. Since the atomization energy of THF is roughly 1300 kcal/mol, an error of even 1% is well outside our target accuracy.

The missing effect of perturbative triples in THF-2-yl and THF-3-yl was estimated by exploiting the available data for THF. As can be seen in Figure 1, where data for six molecules is plotted, the ratio $\Delta E_{(T)}/\Delta E_{SD}$ of the triples correlation energy to the singles and doubles energy is a smoothly varying function of the basis set index ($i = 2$ (DZ), 3 (TZ), etc.). Furthermore, the ratio for a given molecule M, $R(i)^{M}$, is well described by an exponential function. Although we will not exploit this feature in the present work, it can be used to accurately estimate the contribution of triple excitations with a quintuple-ζ basis set when only E_{CCSD} is available. The ratios for THF, THF-2-yl, and THF-3-yl are seen to be nearly identical. If we assume that $R(i)^{THF-2-yl}$, or the corresponding curve for the THF-3-yl radical, can be obtained simply by shifting $R(i)^{THF}$ by some small amount δ, we can use the resulting expression, plus the directly computed value of $\Delta E_{CCSD/VQZ}$ to estimate $E_{CCSD(T)}$.

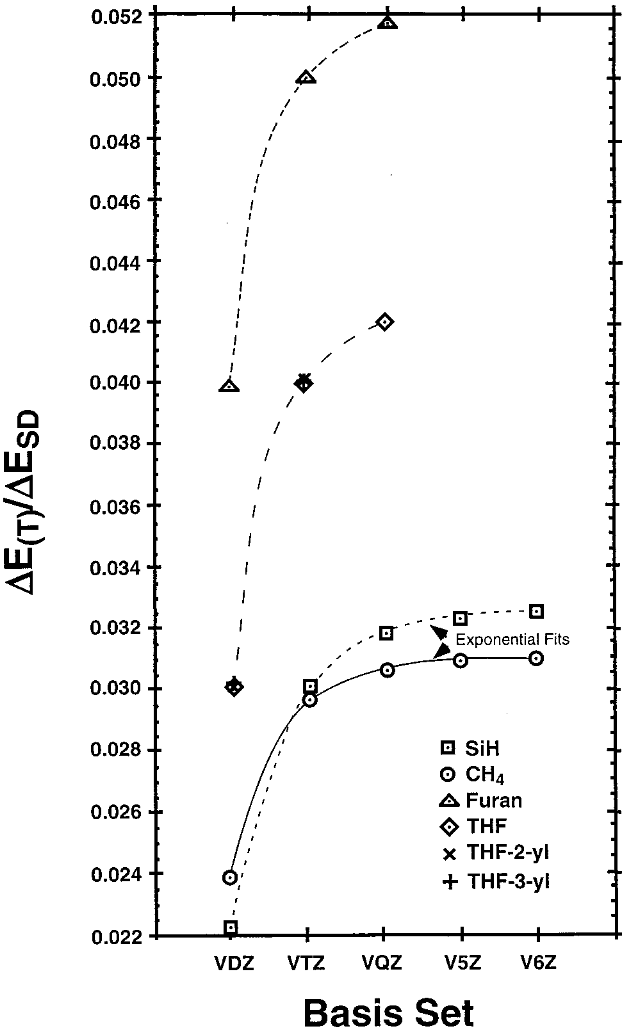

Figure 1. The ratio of the coupled cluster triples correlation energy to the single and doubles contribution as a function of basis set size.

As a test of the accuracy of this approach, we estimated the VQZ triples contribution for furan from the $R(i)$ curve for THF. The estimated value of $\Delta E_{(T)}$ was 0.00019 E_h (0.1 kcal/mol) larger than the actual value. From Figure 1, there is a much larger gap between the THF and furan ratios than between THF and the two radicals. Thus, we would expect the error in the $\Delta E_{(T)}$ estimate for furan to be larger than the corresponding errors for the two radicals.

Although quadruple-ζ basis sets are large by the standards of only a few years ago, atomization energies computed with such basis sets still suffer from a significant basis set truncation error. This error can be reduced by utilizing one of several CBS extrapolations. The earliest to be proposed was an empirically based, simple exponential function of the form

$$E(x) = E_{CBS} + b\exp(-cx) \qquad (1)$$

where x = 2(DZ), 3(TZ), 4(QZ), and $E(x)$ is the corresponding total energy.[45−47] Among the alternative expressions is a mixed exponential/Gaussian function of the form[48]

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

which we′have found to provide better results for ΣD_e than the exponential and slightly better than the third extrapolation to be described, although the differences are small. The final formula is based on the perturbation theory convergence properties of a 2-electron system[49] and involves the reciprocal of $l_{\max}$, the highest angular momentum in the basis set:[50]

$$E_{\text{corr}}(l_{\max}) = E_{\text{CBS}} + B/(l_{\max} + 1)^4 \tag{3}$$

Note that for elements Li−Ar, x (eqs 1 and 2) = $l_{\max}$ (eq 3), when using the correlation consistent basis sets. Although E_{corr} in eq 3 is just the correlation component of the total energy, it is possible to use this expression for the total energy without adversely affecting the performance of the extrapolation because the correlation energy lowering overwhelms the Hartree−Fock energy lowering for large basis sets. If we limit ourselves to basis sets that are no larger than quadruple-ζ, the exponential fit will normally predict the smallest atomization energies, whereas eq 3 produces the largest. The mixed expression gives values that lie somewhere in between. We will adopt the extrapolated energies obtained from the mixed CBS extrapolation (eq 2) as our best estimate and take the spread among the three extrapolations as a crude gauge of the uncertainty in the extrapolation.

Most correlated ab initio calculations do not include the atomic inner shell electrons in the correlation treatment under the assumption that they lie too low in energy to contribute to the formation of chemical bonds. Frozen core (FC) coupled cluster calculations are able to reproduce experimental atomization energies reasonably well, especially for di- and triatomics. However, to achieve so-called “chemical accuracy” (±1 kcal/mol) for larger molecules it is necessary to consider several additional effects that can easily contribute more than 1 kcal/mol to ΣD_e, especially as the size of the molecule under consideration increases.

The first and largest of these corrections is associated with the change in core/valence correlation between the molecule and its constituent atoms. For molecules of the size of THF, this correction, ΔE_{CV}, can easily exceed 5 kcal/mol. For even larger molecules, such as benzene, ΔE_{CV} can exceed 7 kcal/mol. In recognition of the importance of core/valence correlation to the accurate prediction of thermochemical properties, G3 became the first of the Gaussian-x methods to explicitly include core/valence effects. In our previous work, we determined ΔE_{CV} via fully correlated CCSD(T) calculations with the cc-pCVTZ and cc-pCVQZ basis sets,[51] which have been specifically designed to describe these effects. By using both basis sets, it was possible to judge the degree of convergence in ΔE_{CV}. While we adopted the same approach for furan, we were unable to carry out CCSD(T)/cc-pCVQZ calculations on the other three systems. Instead, the cc-pCVTZ result was scaled (up) by the ratio of the CVQZ/CVTZ values of ΔE_{CV} in furan. The CVTZ values differed by less than 0.1 kcal/mol among the four systems.

Additional corrections to ΣD_e were applied in order to account for (1) scalar relativistic effects, (2) “higher order” correlation effects, and (3) atomic spin−orbit effects. The differential scalar relativistic correction ΔE_{SR} was obtained from single and double excitation configuration interaction wave functions using the cc-pVTZ basis set. $\Delta \text{E}_{\text{SR}}$ includes the mass−velocity and one-electron Darwin terms from the Breit−Pauli Hamiltonian.

Several recent studies[52,53] have shown that for molecules that are well described by a single configuration wave function, replacing the perturbative treatment of triple excitations with the more expensive fully iterative treatment, via the method known as CCSDT, can provide results that are slightly closer to the full configuration interaction result. Because of the very high cost of CCSDT, which scales as n,[8] where n is the number of basis functions, we have estimated this “higher order” correlation correction ΔE_{HO} for all four systems by performing CCSDT/VTZ calculations on furan. All CCSDT calculation were performed with the ACES II program.[54]

Most electronic structure packages do not correctly describe the lowest energy spin multiplet of an atomic state, such as the ^{3}P state of carbon. Instead, the energy from these programs corresponds to a weighted average of the available multiplets. To correct for this effect, we apply an atomic spin−orbit correction of −0.08 kcal/mol for each carbon atom and −0.22 kcal/mol for oxygen based on the excitation energies reported by Moore.[55] The sign of the correction is negative, indicating that when added to the theoretical value of ΣD_e, the binding energy *decreases*, since the energy of the atoms was overestimated without the correction.

Three coupled cluster methods are available for handling open shell chemical systems. When dissociating an open shell molecule to open shell atoms, it makes little difference which method is used. However, if the molecule possesses a closed shell electronic configuration, the cumulative effect of the small differences in the atomic energies can be significant. The three methods are characterized by the nature of the reference wave function. If an unrestricted Hartree−Fock (UHF) wave function is used, the method is designated UCCSD(T) in the present work. The other two methods begin with restricted open shell Hartree−Fock (ROHF) orbitals. The method which is completely spin restricted, will be denoted as RCCSD(T).[56−58] The other relaxes the spin constraint in the coupled cluster calculation and will be referred to as R/UCCSD(T).[59,39] The latter method is requested in MOLPRO by the keyword “UCCSD(T)”. Since R/UCCSD(T) atomic energies lie somewhere between the UCCSD(T) and RCCSD(T) extremes, we will only quote results for the latter.

Furan

In our previous work, coupled cluster energies used for computing atomization energies were evaluated at CCSD(T)-optimized geometries with the same basis set. This approach proved to be impractical for the three low-symmetry molecules examined in the present work. For these systems, MP2 was the highest level of theory that could be afforded in geometry optimizations with large basis sets. For comparison purposes, both approaches were followed for furan (^{1}A$_1$). The optimized MP2/VxZ and CCSD(T)/aVxZ geometries are shown in Figure 2, along with the available experimental information.[60] The MP2 geometries were obtained using the “tight” convergence criterion (1.5×10^{-5} E_h/a$_o$) in Gaussian-94.[61] The CCSD(T) geometries were converged to 1×10^{-5} E_h/a$_o$ or better with Gaussian or MOLPRO. At the triple or quadruple-ζ basis set level, perturbation theory and coupled cluster theory both provide good overall agreement with experiment. The largest difference between theory and experiment is a 0.006 Å underestimation of the C−C bond at the MP2/VQZ level.

Table 1 contains the furan frozen core MP2 and CCSD(T) total energies and the corresponding values of ΣD_e. As is typically the case, MP2 drastically overestimates ΣD_e, by 32 kcal/mol at the quadruple-ζ basis set level, relative to the more accurate CCSD(T) method and experiment. Results are presented in Table 1 for atomization energies relative to both RCCSD(T) and UCCSD(T) atomic states. Use of the RCCSD(T) method can be seen to increase ΣD_e by 0.9 kcal/mol, a nontrivial amount in view of the ±1 kcal/mol accuracy target. In light of our recent work on hydrocarbons up through benzene,[41] where RCCSD(T) and UCCSD(T) methods were compared, we adopt the atomization energies obtained with RCCSD(T) atoms as our best estimates.

TABLE 1: Total Energies (E_h) and Vibrationless Atomization Energies (kcal/mol

molecule	symmetry	basis	method[a]	geometry	energy	UHF[b] ΣD_e	ROHF[c] ΣD_e
C_4H_4O ($^1A_1$) furan	C_{2v}	VDZ	MP2	MP2/VDZ	−229.35223	946.1	
		VTZ		MP2/VTZ	−229.57627	996.6	
		VQZ		MP2/VQZ	−229.64957	1012.5	
		VDZ	RCCSD(T)	MP2/VTZ	−229.40758	915.5	915.8
		VTZ		MP2/VTZ	−229.63483	965.5	966.2
		VQZ		MP2/VTZ	−229.70247	980.8	981.6
		aVDZ		CCSD(T)/aVDZ	−229.45128	921.7	922.1
		aVTZ		CCSD(T)/aVTZ	−229.65122	969.9	970.7
		aVQZ		CCSD(T)/aVQZ	−229.70898	982.9	983.8
C_4H_8O (^1A) THF	C_2	VDZ	MP2	MP2/VDZ	−231.73653	1189.1	
		VTZ		MP2/VTZ	−231.97970	1250.2	
		VQZ		MP2/VQZ	−232.05670	1268.1	
		VDZ	RCCSD(T)	MP2/VTZ	−231.81270	1171.6	1171.8
		VTZ		MP2/VTZ	−232.05821	1231.6	1232.3
		VQZ		MP2/VTZ	−232.12882	1248.4	1249.2
		aVDZ		CCSD(T)/aVDZ	−231.86629	1183.8	1184.7
		aVTZ		MP2/VTZ	−231.07644	1237.2	1238.0
C_4H_7O (^2A) THF-2-yl	C_1	VDZ	MP2	MP2/VDZ	−231.08541	1093.2	
		VTZ		MP2/VTZ	−231.32306	1151.8	
		VQZ		MP2/VQZ	−231.39644	1167.5	
		VDZ	RCCSD(T)	MP2/VTZ	−231.15979		1075.4
		VTZ		MP2/VTZ	−231.39912		1132.4
		VQZ		MP2/VTZ	−231.4687[d]		1148.7
C_4H_7O (^2A) THF-3-yl	C_1	VDZ	MP2	MP2/VDZ	−231.07553	1087.6	
		VTZ		MP2/VTZ	−231.31249	1145.2	
		VQZ		MP2/VQZ	−231.38810	1162.2	
		VDZ	RCCSD(T)	MP2/VTZ	−231.15089		1069.5
		VTZ		MP2/VTZ	−231.39083		1127.2
		VQZ		MP2/VTZ	−231.4609[d]		1143.8

[a] When the method is not explictly listed, it defaults to the preceding method. The frozen core approximation was used for all calculations in this table. [b] The atomic dissociation products are described with a UHF reference wave function, i.e., UMP2 or UCCSD(T). [c] The atomic dissociation products are described with a ROHF reference wave function, i.e., RCCSD(T). [d] Based on a CCSD/VQZ calculation and an estimate of the triples contribution to the energy, as described in the text.

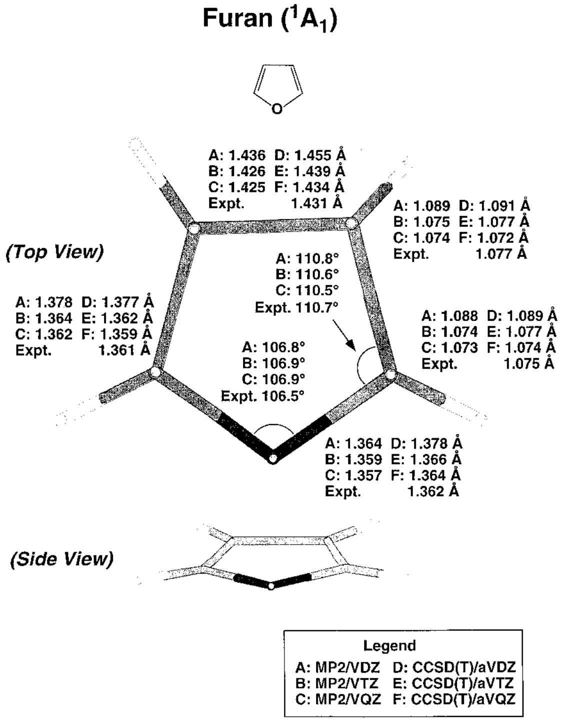

Figure 2. MP2/VxZ- and CCSD(T)/aVxZ-optimized structural parameters for furan and the comparable experimental values.

Up through the quadruple-ζ level, the presence of diffuse functions in the basis set is seen to have an even larger effect on the ΣD_e than the choice of open shell method. At the quadruple-ζ level, the additional functions in the aVQZ basis set result in an extra 2.1 kcal/mol of binding relative to the VQZ basis. As expected, the difference in atomization energies between basis sets with and without diffuse functions decreases as the size of the basis set increases. At the true CBS limit, where both basis set sequences must ultimately produce identical results, our CBS *estimates* obtained via eq 2 differ by 0.7 kcal/mol. Because the augmented sequence of basis sets is, level by level, a more complete set, we assume that the CBS(FC)/aDTQ represents our best estimate of the true CBS limit. The CBS extrapolated frozen core RCCSD(T) values of ΣD_e obtained from both the VDZ → VQZ and aVDZ → aVQZ basis set sequences are listed in Table 2.

The furan zero-point energy (ZPE) vibrational correction was based on the average of $^1/_2\Sigma\nu_i$ and $^1/_2\Sigma\omega_i$, where ν_i are the experimental fundamentals[62] and ω_i are the harmonic CCSD(T)/aVDZ frequencies. The former value is expected to underestimate the true ZPE, while the latter should be an overestimate. Combining the frozen core CBS atomization energy with the ZPE and the four smaller corrections, we obtain a final zero-point-inclusive atomization energy, ΣD_0, of 950.0 ± 0.5 kcal/mol, which encompasses the 950.6 ± 0.2 kcal/mol experimental value reported by Pedley.[63] The corresponding G2, G3, and CBS-Q values all fall within 0.4 kcal/mol of our best estimate, despite differences in ZPE of 0.5 kcal/mol and the absence of corrections such as ΔE_{CV} (G2 and CBS-Q) and ΔE_{SR} (G2, G3 and CBS-Q). It should be noted that furan is a member of the G2/97 training set for G3.

Tetrahydrofuran (THF)

Figure 3 shows the optimized MP2 and experimental[64] structural data for THF. The agreement between theory and experiment is slightly poorer than what was found in furan, but should be more than adequate for purposes of computing an

TABLE 2: CCSD(T), G2, G3, and CBS-Q Atomization Energies[a]

molecule	method	ΣD_e	ZPE[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{HO}[e]	atomic ΔE_{SO}	total ΣD_0[f]	exptl $\Sigma D_{0(0K)}$[g]
C_4H_4O ($^1A_1$) furan	CBS(FC)/aDTQ	990.9	42.9	5.1	−1.1	−1.7	−0.3	950.0 ± 0.5	950.6 ± 0.2: Pedley
	CBS(FC)/DTQ	990.2	42.9	5.1	−1.1	−1.7	−0.3	949.3	
	G2	992.0	42.4					949.6	
	G3	992.5	42.4					950.1	
	CBS-Q	993.2	43.4					949.8	
C_4H_8O (^1A) THF	CBS(FC)/DTQ	1259.7[h]	72.1	5.1	−1.2	−1.7[i]	−0.3	1189.5 ± 0.7	1189.5 ± 0.2: Pedley
	G2	1260.6	70.6					1190.0	
	G3	1260.0	70.6					1189.4	
	CBS-Q	1261.0	72.2					1188.8	
C_4H_7O (^2A) THF-2-yl	CBS(FC)/DTQ	1158.9[h]	65.6	5.1	−1.2	−1.7[i]	−0.3	1095.2 ± 1.0	1096: Muedas
	G2	1158.8	62.4					1096.4	1097: Laarhoven
	G3	1159.4	62.4					1097.0	1098 ± 1: McMillen
	CBS-Q	1160.2	63.8					1096.4	
C_4H_7O (^2A) THF-3-yl	CBS(FC)/DTQ	1154.2[h]	64.7	5.1	−1.2	−1.7[i]	−0.3	1091.4 ± 1.0	
	G2	1153.5	61.7					1091.8	
	G3	1154.3	61.7					1092.6	
	CBS-Q	1155.0	63.1					1091.9	

[a] Results are given in kcal/mol. The CCSD(T) atomization energies are with respect to RCCSD(T) atomic asymptotes. The CBS extrapolations used a mixed Gaussian/exponential formula, as described in the text. The aVDZ → aVQZ sequence of frozen core energies were evaluated at CCSD(T) geometries, whereas the VDZ → VQZ sequence used optimal MP2/VTZ geometries. For THF-2-yl and THF-3-yl, the perturbative triples were estimated as described in the text. [b] The furan zero-point entries associated with the CBS(FC)/aDTQ and CBS(FC)/DTQ rows were based on the average of $0.5[\Sigma\nu_i] + 0.5[\Sigma\omega_i]$, where ν_i are the experimental fundamental frequencies and ω_i are the CCSD(T) harmonic frequencies. The THF ZPE for the row labeled CBS(FC)/DTQ is based on an average of experimental fundamentals and scaled MP2/VDZ harmonic frequencies. The scale factor was 0.9888. For THF-2-yl and THF-3-yl the ZPEs were obtained from scaled MP2/VDZ calculations. [c] Core/valence correction based on CCSD(T)/CVQZ calculations. [d] Scalar relativistic correction based on CISD/VTZ calculations. [e] Higher order correlation correction based on CCSDT/VTZ calculations. [f] Using the frozen core aVDZ → aVQZ CBS extrapolation for furan and the VDZ → VQZ extrapolations for the other molecules. [g] Experimental values are taken from furan and THF = Pedley, ref 63; THF-2-yl = Muedas, ref 6; Laarhoven, ref 7; McMillen = ref 5. [h] Contains a 1.0 kcal/mol correction based on the difference between the aVxZ and VxZ calculations for THF and furan, as described in the text. [i] Adopted from the CCSDT/VTZ value for furan.

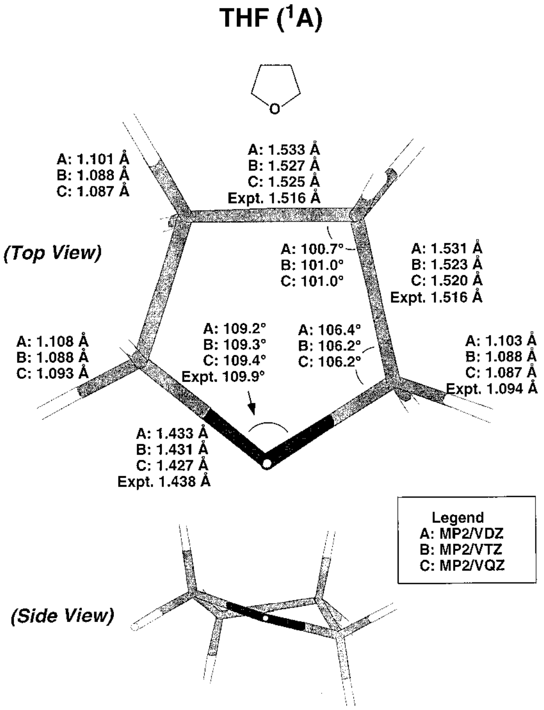

Figure 3. MP2/VxZ-optimized structural parameters for THF and the comparable experimental values.

atomization energy to ±1 kcal/mol. Previous experience has shown that the use of MP2/VTZ geometries when computing CCSD(T) atomization energies, instead of resorting to the much more expensive CCSD(T) geometries, results in a small (0.2−0.4 kcal/mol) effect on the final results.[30,34,65]

As previously mentioned, the ZPE for furan was based on the average of the $^1/_2\Sigma\nu_i$(exptl) and $^1/_2\Sigma\omega_i$(CCSD(T)/aVDZ) vibrational energies. Since it was prohibitively expensive to compute CCSD(T)/aVDZ harmonic frequencies for THF, we scaled the MP2/VDZ frequencies by 0.9888, a scale factor based on the ratio of MP2 to CCSD(T) ZPEs for furan. Therefore, the final THF zero-point vibrational energy was based on the average of $^1/_2\Sigma\nu_i$(exptl) and $^1/_2\Sigma\omega_i$(MP2/VDZ-scaled) vibrational energies.

We were unable to carry out a core/valence calculation for THF with the large CVQZ basis set. Since the smaller CVTZ basis set predicted a ΔE_{CV} correction for THF that differed by only 0.01 kcal/mol from the value found with furan, we adopted the 5.1 kcal/mol CVQZ furan correction for THF.

It was desirable to compare the CBS estimate obtained from the diffuse function augmented sequence of basis sets with the estimate obtained without those functions being present. This information would have been useful for calibrating the CBS/DTQ estimates for the two radicals. However, despite several attempts, it proved impossible to perform a CCSD(T)/aVQZ calculation on THF. For furan, the CBS/DTQ and CBS/aDTQ estimates differed by 0.7 kcal/mol. For THF, the aVDZ−VDZ and aVTZ−VTZ differences in atomization energy are larger than they were in furan, suggesting that the difference in the CBS extrapolated values will also be somewhat larger. On the basis of the aVTZ vs VTZ difference, we estimate that the CBS-(FC)/DTQ value for ΣD_e will be ~1.0 kcal/mol too small. Therefore, the ΣD_e value for THF that is listed in Table 2 includes an increase of 1.0 kcal/mol, to reflect this effect. A similar correction was applied to the THF-2-yl and THF-3-yl atomization energies.

The final CBS binding energy, including all corrections, is $\Sigma D_0 = 1189.5 \pm 0.7$ kcal/mol, in fortuitously perfect agreement with the experimental measurement reported by Pedley.[63] As was the case for furan, the present error bars encompass the G2, G3 and CBS-Q values, which vary by 1.2 kcal/mol, compared to a spread of 0.7 kcal/mol for furan. The small spread in values among the parametrized methods comes despite a

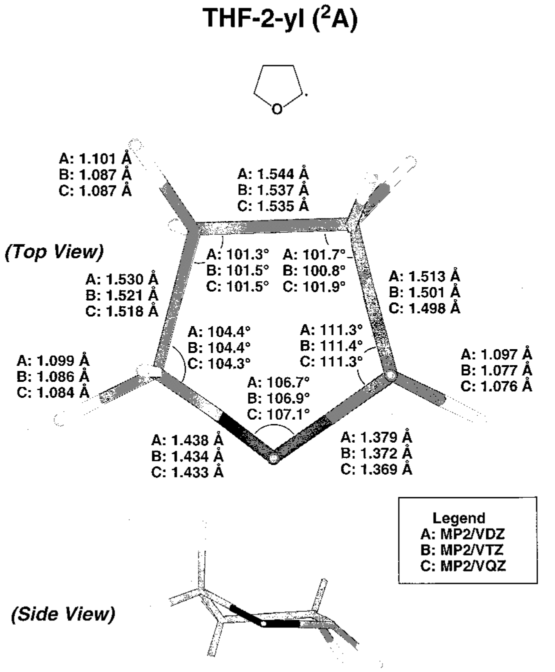

Figure 4. MP2/VxZ-optimized structural parameters for THF-2-yl.

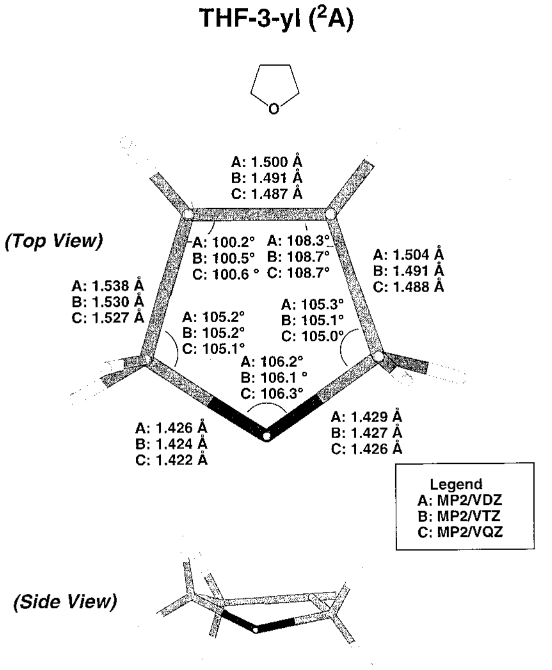

Figure 5. MP2/VxZ-optimized structural parameters for THF-3-yl.

TABLE 3: Theoretical and Experimental Heats of Formation (kcal/mol)

molecule	this work	exptl	exptl tef.[a]
C_4H_4O ($^1A_1$) furan	−4.6 ± 0.5	−5.2 ± 0.2	Pedley
	(−7.7 ± 0.5)	(−8.3 ± 0.2)	
C_4H_8O (^{1}A) THF	−37.6 ± 0.7	−37.6 ± 0.2	Pedley
	(−44.0 ± 0.7)	(−44.0 ± 0.2)	
C_4H_7O (^{2}A) THF-2-yl	5.1 ± 1.0	5.4 (−0.2)	Muedas
	(−0.5 ± 1.0)	2.5 (−3.1)	Laarhoven
		1.5 (−4.1)	McMillen
C_4H_7O (^{2}A) THF-3-yl	8.9 ± 1.0		
	(3.6 ± 1.0)	(1.5−2.5)[b]	Pedley[b]

[a] Experimental heats of formation at 0 K (298 K values in parentheses) are taken from Pedley, ref. [63]; Muedas value corrected by +3.1 kcal/mol, ref. [6]; Laarhoven value, corrected by +1 kcal/mol, ref. [7]; McMillen, ref. [5]. The temperature conversions are based on standard thermochemical expressions that include the 0 → 298 K changes in enthalpy of formation for the atoms and vibrational corrections utilizing the theoretical harmonic frequencies. [b] Range of values corresponding to BDE values of cyclopentane (97.6) to $(CH_3)_2C-H$ (98.6).

variation in zero-point energies of 1.6 kcal/mol and the neglect of core/valence and atomic spin−orbit effects in two of the three methods. The inherent uncertainty in the CCSD(T) value effectively eliminates it as a basis for discriminating among the three parametrized methods. The level of agreement between theory and experiment for furan and THF, as well as the recent results for a series of hydrocarbons,[41] suggests that the present composite approach is capable of achieving the target accuracy of ±1 kcal/mol for organic molecules similar to furan and THF.

THF-2-yl and THF-3-yl

The unrestricted Hartree−Fock-based MP2-optimized geometries of the THF-2-yl and THF-3-yl radicals are shown in Figures 4 and 5. The $\langle S^2 \rangle = 0.76$, indicating only a small amount of spin contamination. A comparison of the THF structure with the structures of the radicals reveals that the only significant difference appears in the vicinity of the respective radical centers. In THF-2-yl the C2−O bond length contracts by 0.06 Å, becoming almost identical with the 1.357 Å MP2 value in furan. For THF-3-yl the biggest change occurs in the CC bond that is opposite the oxygen atom, which shortens by 0.038 Å.

As previously discussed, we were unable to carry out CCSD(T)/VQZ calculations on either radical because of the large number of basis functions and the lack of exploitable symmetry. Approximate CCSD(T)/VQZ energies were obtained by combining the estimated value of the perturbative triples at the quadruple-ζ basis set level with the computed CCSD/VQZ energies. The corresponding CBS extrapolated atomization energies are listed in Table 2. While there are no direct gas-phase measurements of the heats of formation for THF-2-yl or THF-3-yl, several solution phase values for the bond dissociation energy (BDE) of the 2-H in THF are available in the literature.[6,7,5] The present ΣD_0 value of 1095.2 ± 1.0 kcal/mol is in reasonable agreement with the experimental data, which varies from 1096 to 1098 kcal/mol.

The three parametrized models are in good agreement with the coupled cluster results. They predict atomization energies that are within 2 kcal/mol for THF-2-yl and within 1 kcal/mol for THF-3-yl. Given the uncertainty in the CCSD(T) value (± 1 kcal/mol), it cannot be used to discriminate among the G2, G3, or CBS-Q approaches for either radical. In light of the small spread in values for the parametrized methods, the CBS-Q method is to be preferred because of its relatively small computational cost. The G2 calculation on THF-2-yl required 88 h on an SGI Origin 2000, compared to 34 h for G3 and just 11 h for CBS-Q.

Theoretical and experimental 0 K heats of formation are compared in Table 3. The theoretical values are based on the atomic heats of formation taken from the 0 K JANAF values.[66] In lieu of experimental data, we attempted to gauge the accuracy of our THF-2-yl and THF-3-yl atomization energies by applying the same computational strategy to furan and THF, where gas-phase experimental measurements are available. Since the THF-2-yl and THF-3-yl radicals differ from THF by a single C−H bond and the theoretical ΔH_f^0(THF) was in good agreement with experiment, another independent check on the likely accuracy of our approach is our ability to predict the C−H bond dissociation energy (BDE) in a related reaction involving methanol:

TABLE 4: Theoretical and Experimental Reaction Enthalpy (kcal/mol) for $CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$

method	basis	$\Delta H_{\mathrm{rxn}\,(0\,\mathrm{K})}$	$\Delta H_{\mathrm{rxn}}^{\mathrm{exptl}}$(0 K)
UCCSD(T)[a]	aVDZ	7.2	9.0 ± 0.7
	aVTZ	8.2	
	aVQZ	8.4	
	CBS	8.5	
G2		7.8	9.0 ± 0.7
G3		7.7	
CBS-Q		8.1	

[a] UCCSD(T) was used for the open shell systems. ΔH_{rxn} includes a correction for core/valence correlation effects.

$$CH_3OH + CH_3 \rightarrow CH_2OH + CH_4 \qquad (4)$$

Experimental heats of formation at 0 K are available for all species: $\Delta H_f^{\,0}(CH_3OH) = -45.4 \pm 0.1$,[67] $\Delta H_f^{\,0}(CH_3) = 35.6 \pm 0.2$ kcal/mol,[66] $\Delta H_f^{\,0}(CH_2OH) = -2.8 \pm 0.3$ kcal/mol,[68] and $\Delta H_f^{\,0}(CH_4) = -15.99 \pm 0.08$ kcal/mol. The error bars for methanol were based on the error bars quoted by Green.[69] The overall enthalpy of reaction ΔH_{rxn} is 9.0 ± 0.7 kcal/mol, where we have assumed no fortuitous cancellation of errors.

High quality coupled cluster atomization energies, obtained from the same procedure followed in this work, are available for CH_3OH, CH_3, and CH_4.[35,41] The level of agreement with 0 K experimental heats of formation is within ± 0.3 kcal/mol. New coupled cluster calculations were performed on CH_2OH in order to compute ΔH_{rxn} for eq 4. The results are shown in Table 4.

The convergence in ΔH_{rxn} with respect to the size of the basis set is rapid, with even the aVTZ result falling within 0.3 kcal/mol of the CBS limit. Compared to the complete atomization energy of THF, it is much easier to converge the C−H BDE. This finding is in accord with the work of Peterson and Dunning for BDEs in the CH_n and C_2H_n series of hydrocarbons.[70] The CBS value, 8.5 kcal/mol, falls within the 9.0 ± 0.7 kcal/mol experimental error bars, strengthening the notion that the energies of THF-2-yl and THF-3-yl relative to THF should be accurate to within ±1 kcal/mol. Also shown in Table 4 are results for the G2, G3, and CBS-Q model chemistries, which are seen to be in slightly worse agreement with experiment, falling just outside the experimental error bars. The calculation values of $\Delta H_{f,298}$(THF-2-yl) are higher by 2−2.5 kcal/mol than the values estimated from PAC results. However, the error of the PAC values may be several kcal/mol in magnitude.

Conclusions

A variety of theoretical methods have been applied to the atomization energies of four related organic compounds, furan, THF, THF-2-yl, and THF-3-yl. The composite, nonparametrized approach followed in this work relied on large basis set CCSD(T) calculations, followed by an extrapolation to the complete basis set limit. Corrections were applied for core/valence, scalar relativistic, atomic spin−orbit, and higher order correlation effects. Good agreement was found with the available gas-phase experimental data for furan and THF. The accuracy of this approach was limited in the present study by the high computational cost of coupled cluster calculations on systems with little or no exploitable symmetry. As faster processors become available or efficient parallel CCSD(T) implementations are developed, the feasibility of applying this approach to chemical systems such as THF-2-yl and THF-3-yl should improve.

Equally good agreement with experiment was found for the three parametrized methods considered here, G2, G3, and CBS-Q. In view of the considerable difference in computational cost, the G3 and CBS-Q methods provide an attractive alternative to high-level, nonparametrized approaches. On the basis of the results of this study, they should provide equivalent levels of accuracy as their more expensive counterparts for molecules that are chemically similar to the ones considered here.

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