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Predicting the Heats of Formation of Model Hydrocarbons up to Benzene

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The heats of formation of benzene and seven other small hydrocarbons (allyl, allene, cyclopropene, propene, propyne, cyclopropane, and propane) have been calculated at high levels of ab initio molecular orbital theory. Geometries and frequencies were determined, in general, with coupled cluster theory, including a perturbative treatment of the connected triple excitations and with basis sets up through augmented quadruple-ζ in quality or, in some cases, augmented quintuple-ζ. Subsequent extrapolation of the total energies to the complete 1-particle basis set limit was performed, in an effort to further reduce the basis set truncation error. Additional improvements in the atomization energy were achieved by applying corrections for core/valence correlation, scalar relativistic, atomic spin−orbit, and higher-order correlation effects. Zero-point energies were based on an average of the vibrational energies obtained from the experimental fundamentals and theoretical harmonic frequencies. Using restricted open shell treatments for the atoms, we find the following heats of formation (kcal/mol) at 0 K: ΔH_f(allene) = 48.1 ± 0.5 (calcd) vs 47.4 ± 0.3 (expt); ΔH_f(cyclopropene) = 70.5 ± 0.5 (calcd) vs 68.3 ± 0.6 (expt); ΔH_f(propyne) = 46.5 ± 1.5 (calcd) vs 46.0 ± 0.2 (expt); ΔH_f(cyclopropane) = 17.4 ± 1.5 (calcd) vs 16.8 ± 0.1 (expt); ΔH_f(propane) = −20.0 ± 1.6 (calcd) vs. −19.6 ± 0.1 (expt); ΔH_f(propene) = 8.2 ± 1.5 (calcd) vs 8.4 ± 0.2 (expt); ΔH_f(allyl) = 42.7 ± 1.5 (calcd) vs 42.7 ± 0.5 (expt); and ΔH_f(benzene) = 24.7 ± 3 (calcd) vs 24.0 ± 0.2 (expt).

Introduction

Small organic hydrocarbons have played a central role in the development of important chemical concepts, such as resonance stabilization and strain energies, and have been crucial in the development of approximate thermochemical models such as group additivity.[1] In addition, hydrocarbons of the size examined in this study represent some of the simplest molecules that can serve as models for more complicated hydrocarbons relevant to combustion systems. Although the heats of formation of most stable hydrocarbons are well-established,[2−4] there is less high-quality thermodynamic data with respect to reactive intermediates and for larger compounds $>C_{10}$, which are important in the combustion of diesel fuel, as well as in the formation of particulate matter from combustion processes. In addition, as the size of the hydrocarbon grows, the difficulty of experimentally measuring the heats of formation also grows. With the continued rapid increase in computing power, computational methods provide an increasingly attractive alternative for accurate predictions of thermochemical properties.

We have recently begun calibrating a composite theoretical approach that is intended to reliably predict a variety of thermodynamic quantities, including heats of formation, without recourse to empirical parameters.[5−12] As described below, our approach starts with existing, reliable thermodynamic values (obtained from either experiment or theory). Missing pieces of information are then computed by using high-level ab initio electronic structure methods, such as coupled cluster methods including single, double, and connected triple excitations, with the latter being handled perturbatively.[13−15] 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.[10,16]

The Environmental Molecular Sciences Laboratory Computational Results Database[17] currently contains information on the electronic atomization energies, $\sum D_e$, of 139 molecules. An analysis of these results shows that large basis set, frozen core (FC) CCSD(T) calculations display a mean absolute deviation with respect to experiment of ∼3 kcal/mol. However, the maximum error is almost −15 kcal/mol and is associated with the benzene molecule. After extrapolating to the complete basis set (CBS) limit, in an effort to further reduce the magnitude of the finite basis set (1-particle) error, the mean absolute deviation drops to ∼1 kcal/mol and the maximum error to −5.7 kcal/mol (again, benzene). To obtain still better agreement with experiment, corrections for core/valence correlation, atomic spin−orbit effects, molecular scalar relativistic effects, and the remaining correlation energy are required. In addition, vibrational zero-point energies (ZPEs) must also be carefully considered, as significant errors can inadvertently be introduced through the casual adoption of low-level estimates of vibrational contributions to heats of formation. The composite approach that we have developed has been shown to yield reliable atomization energies for a growing number of molecules and is similar to the general approaches followed by Martin[18,19] and Bauschlicher and co-workers.[20,21]

The widely used Gaussian-X model chemistries[22−24] differ from the present approach in the following ways: (1) Gaussian-2 (G2) and Gaussian-3 (G3) atomization energies are dependent on an empirical correction factor obtained by minimizing the atomization energy error with respect to a collection of experimental data; (2) G2 and G3 zero-point energies are obtained from scaled Hartree−Fock frequencies rather than from

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large basis set, correlated calculations or from appropriate experimental results; and (3) with the exception of G3, core/valence and atomic spin−orbit effects are not explicitly included. In contrast, our approach attempts to explicitly account for all contributions to the atomization energies known to contribute ∼1 kcal/mol or more to molecules composed of elements with $Z \leq 18$. G3 is the first of the Gaussian-X models to include core/valence and atomic spin−orbit effects other than implicitly via the "higher order correction". However, it still neglects scalar relativistic effects, which can be as large as 2 kcal/mol for the class of molecules we intend to study. A disadvantage of our more computationally demanding approach as compared to G2 and G3 is that the size of the chemical systems to which it can be applied is, consequently, more limited. Nonetheless, Feller and Peterson[10,16] were able to apply this method to a group of 73 molecules, many of which were taken from the G2 and G2/97 test set, and reported a mean absolute deviation with respect to experiment of 0.7−0.8 kcal/mol.

In the present work we focus on a group of seven C_3 hydrocarbons (allyl, allene, cyclopropane, cyclopropene, propene, propyne, and propane) and benzene, all taken from the G2/97 collection. Of these, benzene represents the largest molecule studied to date by the composite approach described above.

Approach and Results

Our approach relies on the availability of large Gaussian basis sets to use in the so-called 1-particle expansion. For these, we chose the correlation consistent basis sets from Dunning and co-workers[25−29] because of the regularity with which they approach the CBS limit. To treat highly polar molecules and molecular anions, as well as nonpolar hydrocarbons, on an equal footing, most calculations were performed with basis sets that include an additional shell of diffuse functions. These basis sets are conventionally denoted aug-cc-pVxZ, x = D (double), T (triple), etc. However, throughout the text we will abbreviate the basis set labels to aVDZ, aVTZ, etc. Currently available complete basis set extrapolations (described below) require that calculations be carried out through at least the quadruple-ζ level. In several cases, we were able to extend our calculations through the aug-cc-pV5Z level. For even smaller hydrocarbons, it is possible to carry out sextuple-ζ calculations, but the importance of such highly extended basis sets on hydrocarbon energetics at this level has been found to be very small. Only the spherical components (5-d, 7-f, 9-g, and 11-h) of the Cartesian basis functions were used.

As noted above, the primary contribution to $\sum D_e$ is the electronic energy difference between the molecule and the constituent atoms obtained from CCSD(T)(FC) calculations. The largest such calculation performed for this study was a 756 function aug-cc-pVQZ calculation on benzene that required 6.7 days with MOLPRO-97[30] running on a single processor of an SGI Origin 2000. Besides MOLPRO, coupled cluster calculations were also performed with the ACES II[31] and Gaussian 94[32] programs. Most of the work was performed on an SGI Origin 2000, an SGI PowerChallenge, or on an SGI/Cray J90. Some second-order perturbation theory (MP2)[33] geometry optimizations were run with NWChem[34,35] on the 512-node SP2 of the Molecular Science Computing Facility.

Unless otherwise noted, geometries were determined at the CCSD(T) level of theory. Exceptions are benzene with the aug-cc-pVQZ basis set and allene and cyclopropane with the aug-cc-pV5Z basis. Due to the expense of such large basis set CCSD(T) calculations on these systems, the geometry for benzene at the aug-cc-pVQZ level was estimated by adding the aug-cc-pVTZ MP2 → CCSD(T) changes in r_{CC} and r_{CH} to the optimal MP2/aug-cc-pVQZ values of those parameters. The aug-cc-pV5Z bond lengths and bond angles in allene and cyclopropane were extrapolated from the double through quadruple-ζ optimal values using an exponential functional form. As shown in previous work, the use of CCSD(T)-optimized geometries is of only minor importance when computing atomization energies for small molecules, such as those in the G2/97 set. The use of MP2/VTZ geometries causes changes in $\sum D_e$ by no more than a few tenths of a kcal/mol, an amount comparable to, or smaller than, the error introduced by several of the other approximations that are necessary in order to render these calculations tractable. The optimized geometries are summarized in Figure 1 and compared to the available experimental values.

Three coupled cluster methods have been proposed for treating open shell systems. The first is a completely unrestricted method, built atop unrestricted Hartree−Fock (UHF) orbitals and designated UCCSD(T) in the present work. The other two methods start with restricted open shell Hartree−Fock (ROHF) orbitals. One is a completely restricted method, which we will denote as RCCSD(T).[36−38] The other relaxes the spin constraint in the coupled cluster calculation and will be referred to as R/UCCSD(T).[15,39,40] The latter method is requested in MOLPRO by the keyword "UCCSD(T)" when combined with an ROHF wave function. Although energy differences among the various open shell coupled cluster methods are not large, the cumulative effect for some of the molecules was significant in light of the accuracy being sought. Since R/UCCSD(T) atomic energies lie somewhere between the UCCSD(T) and RCCSD(T) extremes, we will only quote results for the latter two.

The raw atomization energies can usually be improved by extrapolating to the CBS limit, especially when the largest basis set is the aVQZ. Experience with smaller systems showed only a small spread in the effectiveness of various CBS extrapolations, but we choose to use a mixed exponential/Gaussian function of the form:

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

where x = 2 (DZ), 3 (TZ), etc., which was first proposed by Peterson et al.[41] As a crude estimate of the uncertainty in the CBS extrapolation, we adopt the spread in the CBS estimates obtained from the mixed expression and two alternative functional forms, a simple exponential:[42,43]

$$E(x) = A_{CBS} + B\exp(-Cx) \quad (2)$$

and an expansion in $1/l_{max}$:

$$E(x) = A_{CBS} + B/(l_{max} + {}^1\!/_2)^4 \quad (3)$$

where l_{max} is the maximum l value for the basis set (? = 0, 1, 2, ... for s,p,d, etc.).[44,45] For second and third row elements, x (eqs 1 and 2) = l_{max} (eq 3), when using the correlation consistent basis sets.

The next largest contribution to the atomization energy is due to the molecular zero-point energy. With the exception of benzene, the harmonic frequencies (ω_i) which were required for computing vibrational ZPEs via the expression

$$\mathrm{ZPE} = \frac{1}{2}\left[\frac{1}{2}\sum \nu_i(\mathrm{expt}) + \frac{1}{2}\sum \omega_i(\mathrm{CCSD(T)/aVDZ})\right] \quad (4)$$

were obtained from CCSD(T)/aVDZ calculations. The ν_i in eq 4 are the experimental fundamentals. The experimental com-

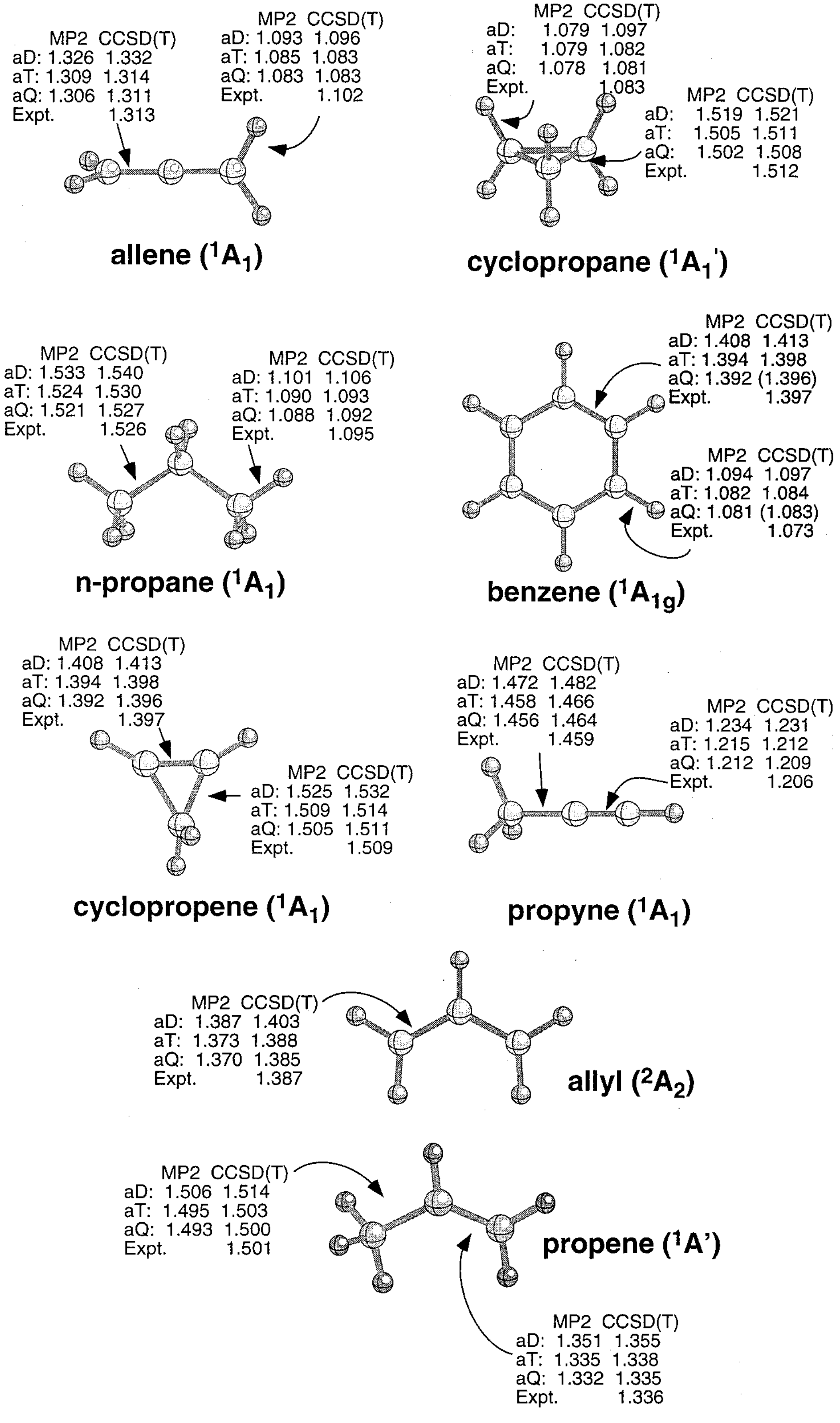

Figure 1. Selected optimized bond lengths and bond angles. aD = aug-cc-pVDZ, aT = aug-cc-pVTZ, etc.

ponent of eq 4 is expected to underestimate the true anharmonic ZPE, while the harmonic component usually overshoots. The benzene harmonic frequencies were taken from the CCSD(T)/VTZ′ values of Martin et al.[46] Of the seven systems examined in this study, all but one had a complete set of experimental frequencies. The allyl radical was the exception, and the missing frequencies were estimated from the calculated values. For allyl, two of the A_1 frequencies, one of the A_2, and one of the B_2 frequencies was missing. In general, the ZPE based on experimental fundamentals and the ZPE based on the CCSD(T) harmonic frequencies fall within 2 kcal/mol of each other. For example, in benzene $0.5*\sum\nu_i(\mathrm{expt}) = 61.1$ kcal/mol and $0.5*\sum\omega_i = 62.4$ kcal/mol. Based on our experience with CH_4, it is likely that the calculated values for benzene are closer to the true ZPE. The experimental frequencies of allene, propyne, propane, and cyclopropane were taken from Shimanouchi.[47] The frequencies for benzene are from Hollinger.[48] The frequencies for cyclopropene are due to Yum and Eggers,[49] and those for

TABLE 1: Theoretical CCSD(T) and Experimental Frequencies (cm^{-1})[a]

molecule	sym	calcd	expt	molecule	sym	calcd	expt
C_3H_4 allene	E	307.9	355	C_3H_4 propyne	E	251.5	328
		843.7	841			539.8	633
		994.1	999			1049.5	1053
		3226.3	3086			1461.1	1452
	B_1	848.2	865			3113.9	3008
	A_1	1067.8	1073		A_1	927.8	931
		1466.2	1443			1390.5	1382
		3134.1	3015			2146.3	2142
	B_2	1417.6	1398			3032.7	2918
		1985.7	1957			3446.3	3334
		3133.3	3007				
C_3H_4 cyclopropene	B_1	527.3	569	C_3H_6 cyclopropane	E″	731.1	739
		1078.2	1088			1198.2	1188
		3133.9	2995			3111.8	3082
	A_2	753.7	769		A_2''	846.9	854
		1000.9	996			3124.8	3102
	B_2	769.1	815		E′	885.6	869
		1012.0	1011			1042.7	1028
		1048.5	1043			1457.5	1438
		3249.6	3116			3197.1	3024
	A_1	910.2	905		A_2'	1060.2	1070
		1143.9	1105		A_1''	1142.9	1126
		1498.8	1483			1213.2	1188
		1658.6	1653			1513.8	1479
		3057.6	2909			3218.2	3038
		3292.6	3152				
C_3H_8 *n*-propane	A_2	234.4	216	C_3H_5 allyl	A_1	418.8	427
		896.2	940			1025.2	1066
		1300.0	1278			1259.5	1245
		1472.3	1462			1510.4	1488
		3079.2	2967			3142.4	3048
	B_1	273.7	268			3155.4	
		737.4	748			3249.3	
		1199.7	1192		B_1	524.7	518
		1491.0	1476			791.1	802
		3047.8	2968			981.0	968
		3088.7	2973		A_2	543.4	549
	A_1	363.9	369			775.5	
		880.0	869		B_2	918.0	1182
		1166.6	1158			1182.3	1389
		1401.5	1392			1403.7	1463
		1471.9	1451			1503.3	
		1489.5	1472			3138.4	3016
		3011.3	2887			3246.8	3105
		3015.2	2962				
		3093.7	2997				
	B_2	914.9	922				
		1070.6	1054				
		1346.1	1338				
		1388.9	1378				
		1476.2	1464				
		3008.7	2887				
		3089.9	2968				
C_3H_6 propene	A′	416.0	428				
		895.8	912				
		926.5	919				
		932.3	935				
		1180.1	1179				
		1397.4	1378				
		1439.3	1420				
		1487.3	1459				
		1681.6	1653				
		3020.7	2932				
		3104.1	2973				
		3125.7	2991				
		3141.5	3017				
		3226.1	3091				
	A″	194.8	188				
		569.4	575				
		990.7	990				
		1058.0	1045				
		1304.3	1298				
		1479.6	1443				
		3092.1	2953				

[a] Harmonic frequencies are based on CCSD(T)/aVDZ calculations. References for the experimental frequencies are Shimanouchi[47] for allene, propyne, propane, propene and cyclopropane; Yum and Eggers[49] for cyclopropene; and Jacox,[50] for allyl.

allyl are from Jacox.[50] The calculated vibrational frequencies are compared to the experimental values in Table 1.

We now discuss a series of corrections to the CCSD(T)(FC) binding energies that are of lesser importance, but are nonetheless still significant when trying to achieve an accuracy of ±1 kcal/mol or better for all molecules. Core/valence corrections to the dissociation energy were obtained from fully correlated CCSD(T) calculations with the cc-pCVTZ and cc-pCVQZ basis sets[51] at either the CCSD(T)/aug-cc-pVTZ or MP2/cc-pVTZ geometries. The cc-pCVQZ basis sets include additional functions that allow for core/valence correlation. Experience has shown that the cc-pCVTZ basis set recovers ~75% or more of the effect seen with the larger cc-pCVQZ basis. By performing calculations with both basis sets, we were able to judge the degree of convergence in the correction. In the following discussion, these corrections will be labeled ΔE_{CV}. For seven of the eight hydrocarbons, the differences in the CVTZ and CVQZ values of ΔE_{CV} were $\leq$ 0.5 kcal/mol, suggesting that the CVQZ result should be converged to ~0.2 kcal/mol or better. Benzene showed the largest difference at 0.9 kcal/mol. Extrapolation of ΔE_{CV} to the CBS limit was not attempted because of the relatively small size of this correction, compared to the total atomization energy, and the apparent degree of convergence in the CVQZ results. Although correcting ΔE_{CV} for the undesirable effects of basis set superposition error (BSSE) would reduce the magnitude of ΔE_{CV}, in every case examined here ΔE_{CV} increased as the basis set was improved. Thus, the raw values of ΔE_{CV} lie closer to the CBS limit than values adjusted (decreased) by BSSE considerations.

The next set of corrections deal with the effect of relativity. Most popular electronic structure packages do not correctly describe the lowest energy spin multiplet of an atomic state, such as the ^3P state of carbon. Instead, the energy is 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 C based on the excitation energies of Moore.[52] The sign of the correction is negative, indicating that when added to the theoretical value of $\sum D_e$, the binding energy decreases, since the energy of the atoms was underestimated without the correction.

Besides atomic spin−orbit effects, there are also scalar molecular relativistic corrections which are intended to account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms. Although fully relativistic, 4-component electronic structure methods are available, they are currently too time-consuming to consider using them on polyatomic molecules of the size of propane or benzene. In previous studies,[10,12,16] we evaluated the scalar relativistic correction, ΔE_{SR}, with single and double excitation configuration interaction wave functions using the cc-pVTZ basis set (CISD/VTZ). The calculations were performed within the frozen core approximation. ΔE_{SR} was represented as the sum of the expectation values of the mass−velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[53] Comparisons between this approach and published 4-component results, or Douglas−Kroll (DK) scalar relativistic corrections, suggested that CISD/VTZ should be accurate to ~ ±0.2 kcal/mol. The number of comparisons was limited due to the scarcity of published 4-component and DK results.

Recently, however, Bauschlicher and Ricca[54] have criticized the use of CISD wave functions and the cc-pVTZ basis set, arguing that such a level does not yield ΔE_{SR} values that are as accurate as we had initially found. In a series of large basis set, Douglas−Kroll modified couple pair functional (DK-MCPF) calculations on CF, CF_4, and SiF_4, they showed that the CISD/VTZ ΔE_{SR} value differed by −0.1 (CF), −0.6 (CF_4) and −0.4 (SiF_4) kcal/mol from their best estimates. In the worse case (CF_4), the error was three times larger than our estimate of the

TABLE 2: The Effects of Variations in the Basis Set and Level of Theory on Molecular Scalar Relativistic Corrections[a]

			ΔE_{SR} (kcal/mol)		
molecule	basis set	method	DK[b]	MVD[c]	ref
CF ($^2\Pi$)	VTZ/aVTZ[e]	MCPF	−0.168	−0.213	Bauschlicher[d]
		CCSD(T)	−0.160		
	VQZ/aVQZ[f]	MCPF	−0.169	−0.144	
	V5Z/aV5Z[g]	MCPF	−0.170	−0.142	
	VTZ	CISD		−0.277	FP
	VQZ	CISD		−0.172	this work
	aVDZ	iCAS-CI		−0.036	
	aVTZ	iCAS-CI		−0.231	
	aVQZ	iCAS-CI		−0.158	
	aV5Z	iCAS-CI		−0.150	
CH ($^2\Pi$)	VTZ	CISD		−0.043	FP
		iCAS-CI		−0.046	this work
	VQZ	iCAS-CI		−0.038	
CH_2 ($^3B_1$)	VTZ	CISD		−0.147	FP
		iCAS-CI		−0.146	this work
	VQZ	iCAS-CI		−0.137	
CH_4 ($^1A_1$)	VTZ	CISD		−0.186	FP
		iCAS-CI		−0.194	this work
	VQZ	iCAS-CI		−0.182	
C_2H_2 ($^1\Sigma_g^+$)	VTZ	CISD		−0.283	
	FP		iCAS-CI		−0.291
this work		aVQZ	iCAS-CI		−0.286
C_2H_4 ($^1Ag'$)	VTZ	CISD		−0.338	FP
		iCAS-CI		−0.345	this work
	VQZ	iCAS-CI		−0.331	

[a] The results of Feller and Peterson (FP), ref 10, and the results labeled "this work" were obtained at the optimal CCSD(T)/aVTZ geometries. Specifically, $r_{CF} = 1.2808$ Å. The CF results of Bauschlicher were obtained at the experimental bond length, $r_{CF} = 1.2718$ Å. [b] DK = Douglas−Kroll. [c] MVD = mass−velocity + Darwin correction. [d] Bauschlicher, ref 54. [e] Mixed basis set with the cc-pVTZ basis set on carbon and the aug-cc-pVTZ set on fluorine. [f] Mixed basis set with the cc-pVQZ basis set on carbon and the aug-cc-pVQZ set on fluorine. [g] Mixed basis set with the cc-pV5Z basis set on carbon and the aug-cc-pV5Z set on fluorine.

inherent accuracy of our approach and, as such, is clearly unacceptable if a target accuracy of ±1 kcal/mol is to be achieved.

The source of the errors varied from molecule to molecule. For CF, it arose from the basis set sensitivity of the MVD approach, whereas for SiF_4 the error appeared to arise mostly from the use of a CISD wave function. In the latter case, CISD calculations with the uncontracted VQZ basis set were still 0.44 kcal/mol larger than the DK-MCPF result with a triple-ζ basis set. Bauschlicher and Ricca showed that in the limit of large basis sets, the MVD and DK approaches gave similar results, but that the DK method appeared to be less sensitive to basis set than the MVD method.

Since we currently do not have access to a computer code capable of Douglas−Kroll calculations, we calibrated the CISD/VTZ MVD approach for a collection of hydrocarbons and CF ($^2\Pi$). Comparisons were made with internally contracted, complete active space configuration interaction (iCAS-CI) results obtained with the VTZ and VQZ basis sets. The results are shown in Table 2, where for CF it can be seen that basis sets of quadruple-ζ level are required to achieve 0.05 kcal/mol convergence, if basis set selection is restricted to the unmodified correlation consistent sets. However, none of the five hydrocarbons shows a similar sensitivity to either the basis set or level of theory. Therefore, we conclude that the CISD/VTZ MVD approach is capable of reproducing the molecular scalar relativistic correction for the systems examined in this study to an accuracy of ±0.1 kcal/mol or better. The findings of Bauschlicher and Ricca demonstrate that for troublesome systems (perhaps highly ionic ones) the error may be larger. Until enough experience can be gained, it will be necessary to check the accuracy of CISD for each new class of molecules. At this point, we have accounted for a variety of correction terms given that the calculation of $\sum D_e$ is dominated by the CCSD(T) energy terms.

The final correction that will be applied is designed to account for the remaining differential correlation energy, i.e., it should approximately account for the difference between our CCSD(T) and a full CI for a given basis set. We therefore refer to it as a "higher order correction" (ΔE_{HO}). It was recently shown[55] that the CCSDT[56−59] method is capable of approximating the energy difference between full CI and CCSD(T) with semiquantitative accuracy. Errors with respect to estimated full CI dissociation energies obtained with quadruple-ζ basis sets ranged from 0.09 kcal/mol for CO to 0.28 kcal/mol for N_2. Both are "difficult" molecules due to the presence of a triple bond. The sign of the correction for these diatomic molecules was negative, i.e., it tended to decrease the binding energy. For the present work, we used the MOLPRO full CI code to perform benchmark calculations on CH ($^2\Pi$) with the cc-pVDZ and cc-pVTZ basis sets. The errors due to use of CCSDT as compared to full CI were −0.06 and −0.07 kcal/mol respectively, compared to differences of the full CI with respect to CCSD(T) of +0.13 and +0.11 kcal/mol. Thus, CCSDT recovered about half of the increase in binding energy found with full CI for this model diatomic, although we note that the errors are only on the order of 0.1 kcal/mol. A much larger number of comparisons between CCSDT and full CI will be needed in order to establish the accuracy of the method. In light of the expense of these methods and the need to use a basis set of triple-ζ quality or better to reproduce the true effect of higher order excitations, this effort will prove to be an extremely challenging computational task.

To estimate the size of ΔE_{HO} for the dissociation energies of some small, previously reported hydrocarbons, we have calculated the value of this correction at the CCSDT/cc-pVTZ level. The magnitude of ΔE_{HO} for the seven small hydrocarbons is shown in Table 3 to be small, but not entirely negligible. The largest effect is found for acetylene with a triple bond where it amounts to −0.56 kcal/mol. The magnitude of ΔE_{HO} is expected to increase with the size of the system. Table 3 also contains the corresponding experimental atomization energies with their stated uncertainties.[2−4,60−63]

The final theoretical atomization energies appearing in Table 3 have been assigned estimated error bars based on the spread in the CBS estimates obtained from eqs 1−3 and on our assessment of the likely errors arising from each of the smaller corrections. These include errors arising from the use of harmonic frequencies (if necessary), the core/valence, scalar relativistic, and higher order correlation corrections. Our error analysis assumes no cancellation of error, although given the variations in sign of the different effects some cancellation is likely to occur.

By combining our computed $\sum D_0$ values with the known[3] heats of formation at 0 K for the elements: $\Delta H_f^0(C) = 169.98 \pm 0.1$ kcal/mol, and $\Delta H_f^0(H) = 51.63$ kcal/mol, we can derive ΔH_f^0 values for the molecules under study. The uncertainties in our theoretical approach are probably large enough that the uncertainties in the experimental heats of formation of carbon are negligible. Nonetheless, as pointed out by Feller and Peterson,[10,16] theory is rapidly approaching the point where the scarcity of highly accurate experimental heats of formation may hinder the calibration of newer methods.

TABLE 3: The Impact of the Higher Order Correction on Previously Reported CCSD(T) Atomization Energies[a]

	CBS/mixed $\sum D_e$									
molecule	(aDTQ)	(aTQ5)	atoms[b]	ZPE[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{HO}[f]	atomic ΔE_{SO}[g]	total $\sum D_0$[h]	expt $\sum D_0$ (0 K)[i]
CH ($^2\Pi$)	83.8	83.8	UCCSD(T)	4.0	0.2	−0.1	0.11	0.0	80.0 ± 0.1	79.90 ± 0.02 HH
										80 ± 4 JANAF
CH_2 ($^3B_1$)	190.5	189.7	UCCSD(T)	10.6	0.8	−0.2	0.01	−0.1	179.7 ± 0.2	179.6 LZ
										181.0 ± 1 JANAF
CH_2 ($^1A_1$)	180.6	180.5	UCCSD(T)	10.3	0.4	−0.1	0.22	−0.1	170.6 ± 0.2	170.6 MBSESS
CH_3 ($^2A_2''$)	306.7	306.5	UCCSD(T)	18.4	1.0	0.0	0.00	−0.1	289.1 ± 0.3	289.3 ± 0.2 JANAF
CH_4 ($^1A_1$)	419.1	418.8	UCCSD(T)	27.7	1.3	−0.2	−0.04	−0.1	392.1 ± 0.3	392.5 ± 0.1 JANAF
	419.3	419.0	RCCSD(T)						392.3 ± 0.3	
C_2H_2 ($^1\Sigma_g^+$)	402.8	402.3	UCCSD(T)	16.5	2.4	−0.3	−0.56	−0.2	387.2 ± 0.4	386.9 ± 0.2 JANAF
	403.2	402.7	RCCSD(T)						387.6 ± 0.4	388.9 WEPSHBCN
C_2H_4 ($^1A_g'$)	561.6	561.0	UCCSD(T)	31.5	2.3	−0.3	−0.32	−0.2	531.0 ± 0.4	531.9 ± 0.1 JANAF
	562.0	561.4	RCCSD(T)						531.4 ± 0.4	
C_2H_6 ($^1A_{1g}$)	710.5	710.0	UCCSD(T)	46.4	2.4	−0.4	−0.25	−0.2	665.2 ± 0.4	666.3 WEPSHBCN
	710.9	710.4	RCCSD(T)						665.6 ± 0.4	

[a] Results are given in kcal/mol. [b] Method used for treating the atomic asymptotes. [c] Zero-point energies were taken from the anharmonic experimental values. [d] Core/valence corrections were obtained with the cc-pCVQZ basis sets at the optimal CCSD(T)/aug-cc-pVTZ geometries. A positive sign indicates that CV effects increase the stability of the molecule relative to the atomic asymptotes. [e] The scalar relativistic correction is based on CISD(FC)/cc-pVTZ calculations of the 1-electron Darwin and mass−velocity terms evaluated at the CCSD(T)(FC)/aug-cc-pVTZ geometry. [f] Higher order correlation correction based on CCSDT/cc-pVTZ calculations at the optimal CCSD(T)/aug-cc-pVTZ geometries. [g] Correction due to the improper treatment of the atomic asymptotes as an average of spin multiplets. For diatomics with a nonzero molecular spin−orbit contribution, e.g., CH (2Π), this is the sum of the atomic and molecular contributions. [h] Using the best available CBS estimate for $\sum D_e$. Error bars for $\sum D_0$ are based, in part, on the uncertainties associated with the CBS extrapolations. "Total $\sum D_0$" is defined as E[CCSD(T)(FC)/CBS]- ZPE + CV + scalar relativistic + higher order correlation + atomic/molecular S.O. [i] Experimental values are denoted as follows: HH = Huber and Herzberg[60]; JANAF = Chase[3]; LZ = Lengel and Zare[62]; MBSESS = McKellar et al.[61]; WEPSHBCN = Wagman et al.[63].

TABLE 4: CCSD(T)(FC) Total Energies (E_h) at the Optimized CCSD(T) Geometries

basis	allene	cyclopropene	propyne	cyclopropane	propane	allyl	benzene	propene
aVDZ	−116.334967	−116.298332	−116.334945	−116.471520	−118.803790	−116.933696	−231.617207	−117.57874
aVTZ	−116.441233	−116.405349	−116.442995	−117.677878	−118.922450	−117.039948	−231.820464	−117.690308
aVQZ	−116.469527	−116.434193	−116.471521	−117.707761	−118.952768	−117.068832	−231.877535	−117.719912
aV5Z	−116.477673	−116.442581						

Discussion

Selected bond lengths and bond angles taken from the optimized MP2 and CCSD(T) structures are shown in Figure 1. Comparison with the available experimental data for benzene,[64] allyl,[65] allene,[66] cyclopropene,[66] propyne,[66] cyclopropane,[67] and propane[68] shows that, for this selection of hydrocarbons, MP2 and CCSD(T) are both capable of predicting r_e values that are in good agreement with the vibrationally averaged experimental values.

The agreement between the calculations and experiment for the frequencies given in Table 1 is reasonable. The calculated C−H stretches are larger by 100 to 150 cm^{-1}, as compared to the experimental values, consistent with the fact that the former are harmonic and the latter contain anharmonic terms. The largest difference is for the A_1 C−H stretch for cyclopropane. The most surprising differences between theory and experiment are seen for the lowest energy modes. For example, the calculated value for the lowest E mode in allene is 47 cm^{-1} too low. The calculated lowest energy B_1 mode in cyclopropene is 32 cm^{-1} too low and the lowest B_2 mode is 46 cm^{-1} too low. The differences in propyne are even more striking with the two lowest energy E modes 76 and 93 cm^{-1} predicted to be too low. In propane, the largest difference is predicted for the second lowest A_2 mode which is 44 cm^{-1} too low.

The level of agreement between theory and experiment found in Table 3 is very high, with dissociation energies falling within the stated error bars for most compounds. We note that for the closed shell molecules, the use of RCCSD(T) atomic energies gives somewhat better agreement with experiment. The largest error occurred in C_2H_2, where the RCCSD(T) value differs from the JANAF value[3] by 0.7 kcal/mol and from the Wagman et al.[63] value by −1.3 kcal/mol. However, the two experimental values differ from each other by 2 kcal/mol and our number thus lies between the two experimental values.

It is useful to examine the size of the smaller contributions to $\sum D_e$. ΔE_{CV} ranges from 0.2 kcal/mol (CH) to 2.4 kcal/mol (C_2H_6), obviously increasing with the number of bonds. The scalar relativistic corrections are all much smaller, varying from 0.0 to −0.4 kcal/mol, with the compounds with two carbons having a larger absolute correction. The higher order corrections range from 0.0 (CH_3) to −0.56 kcal/mol (C_2H_2). Note that the sign of ΔE_{HO} can be either positive or negative for these small hydrocarbons.

Total CCSD(T) energies for the eight hydrocarbons that are the focus of the present work are listed in Table 4. Table 5 contains the theoretical and experimental[2,69] atomization energies, where it can be seen that the two are in good agreement. Here again, RCCSD(T) atomic energies provide slightly better agreement than UCCSD(T). The largest difference is found for cyclopropene. For allene, with two double bonds at 90 degree to each other, the predicted value for $\sum D_0$ is 0.7 kcal/mol smaller than experiment, consistent with the result for C_2H_4 where the predicted value is 0.5 kcal/mol smaller. The predicted value for propyne, an isomer of allene with a triple bond, is also 0.5 kcal/mol below the experimental value. This suggests that the true value for $\sum D_0(C_2H_2)$ may be ~0.5 kcal/mol above the RCCSD(T) value, or ~388.1 kcal/mol. Experimentally, the two low energy C_3H_4 isomers differ by 1.4 kcal/mol, with propyne being more stable. The computational energy difference is 1.6 kcal/mol.

The least stable C_3H_4 isomer that we examined is the strained ring system, cyclopropene. The calculated atomization energy is 2.2 kcal/mol smaller than experiment, whereas for cyclopropane (C_3H_6) this difference drops to 0.6 kcal/mol. The level of

TABLE 5: CCSD(T) Atomization Energies[a]

molecule	CBS/mixed $\sum D_e$ (aDTQ)	(aTQ5)	atoms[b]	ZPE[c]	ΔE_{CV}	ΔE_{SR}	ΔE_{HO}	atomic ΔE_{SO}	total $\sum D_0$[d]	expt $\sum D_0$ (0 K)[e]
C_3H_4 ($^1A_1$)	700.2	699.4	UCCSD(T)	33.7	3.5	−0.5	−0.62	−0.25	667.9 ± 0.5	669.1 ± 0.3 PNK
allene	700.7	699.9	RCCSD(T)						668.4 ± 0.5	
C_3H_4 ($^1A_1$)	678.8	677.6	UCCSD(T)	34.1	3.5	−0.6	−0.87	−0.25	645.5 ± 0.5	648.2 ± 0.6 PNK
cyclopropene	679.3	678.1	RCCSD(T)						646.0 ± 0.5	
C_3H_4 ($^1A_1$)	701.6		UCCSD(T)	33.9	3.3	−0.5	−0.77	−0.25	669.5 ± 1.5	670.5 ± 0.2 PNK
propyne	702.1		RCCSD(T)						670.0 ± 1.5	
C_3H_6 ($^1A_1'$)	850.2		UCCSD(T)	50.0	3.2	−0.6	−0.70	−0.25	801.8 ± 1.5	802.9 ± 0.1 PNK
cyclopropane	850.7		RCCSD(T)						802.3 ± 1.5	
C_3H_6 ($^1A'$)	857.8		UCCSD(T)	48.9	3.4	−0.6	−0.50	−0.25	811.0 ± 1.5	811.3 ± 0.2 PNK
propene	858.3		RCCSD(T)						811.5 ± 1.5	811.4 ± 0.2 FKMRW
C_3H_8 ($^1A_1$)	1004.0		UCCSD(T)	63.7	3.5	−0.6	−0.45	−0.25	942.5 ± 1.6	942.6 ± 0.1 PNK
propane	1004.5		RCCSD(T)						943.0 ± 1.6	
C_3H_5 ($^2A_2$)	762.8		UCCSD(T)	40.6	3.2	−0.5	0.22	-0.25	724.9 ± 1.5	725.4 ± 0.5 Roth
allyl	763.3		RCCSD(T)						725.4 ± 1.5	
C_6H_6 ($^1A_{1g}$)	1362.3		UCCSD(T)	61.8	7.1	−1.1	(−2.1)[f]	−0.50	1303.9 ± 3	1305.7 ± 0.2 PNK
benzene	1363.4		RCCSD(T)						1305.0 ± 3	

[a] Results are given in kcal/mol. [b] Method used for treating the atomic asymptotes. [c] Zero-point energies were taken as the average of $0.5*[\sum \nu_i] + 0.5*[\sum \omega_i]$, where ν_i are the experimental fundamental frequencies and ω_i are the CCSD(T)/aVDZ harmonic frequencies. [d] Using the best available value of $\sum D_e$. [e] Experimental values are taken from PNK = Pedley et al.[2]; FKMRW = Frenkel et al.[4]; Roth.[69] [f] Higher order correction is based on a directly computed CCSDT/pVDZ value of −0.9 kcal/mol and a pVDZ → pVTZ adjustment of −1.2 kcal/mol estimated from the convergence behavior of the CCSDT calculations on cyclopropene.

agreement in the latter case shows that our method can easily handle a highly strained ring system. Thus, the size of the disagreement for cyclopropene is surprising.

For the allyl radical, propane, propene, cyclopropene, and benzene, excellent agreement with experiment was obtained. The differences between the predicted and measured atomization energies are 0.0, +0.4, and −0.7 kcal/mol, respectively. Propane presents the only case in which the theoretical prediction exceeds the experimental value.

The smaller correction terms exhibit some interesting behavior. The core/valence correction ΔE_{CV} is remarkably constant at 3.2 to 3.5 kcal/mol for the C_3 compounds. Consistent with these values, ΔE_{CV} is 7.1 kcal/mol for benzene, a larger number than expected on the basis of simple chemical principles. The scalar relativistic correction show little fluctuation, ranging between −0.5 and −0.6 kcal/mol for the C_3 compounds and −1.1 kcal/mol for benzene. The ΔE_{HO} correction shows a somewhat broader range of behavior, varying from −0.45 kcal/mol for propane to −0.87 kcal/mol for the highly strained cyclopropene. This shows that ΔE_{HO} does not scale just with the number of electrons but also with the types of bonds that are present. For allyl, ΔE_{HO} is small, 0.22 kcal/mol, and of the opposite sign. For benzene, we could not afford to perform a CCSDT/pVTZ calculation, so we estimated the value from a CCSDT/pVDZ calculation on benzene (which gave −0.9 kcal/mol) and an additional adjustment of −1.2 kcal/mol based on the convergence behavior of CCSDT calculations on cyclopropene. This yields a ΔE_{HO} correction estimate of −2.1 kcal/mol for benzene.

TABLE 6: Comparison of Calculated and Experimental Heats of Formation in kcal/mol at 0 K

molecule	ΔH_f(0 K) calcd	ΔH_f(0 K) expt
CH ($^2\Pi$)	141.6 ± 0.1	141.2 ± 4.2
		141.7
CH_2 ($^3B_1$)	93.5 ± 0.2	93.6
		92.2 ± 1
CH_2 ($^1A_1$)	102.6 ± 0.3	102.6 ± 0.2
CH_3 ($^2A_2''$)	36.0 ± 0.3	35.6 ± 0.2
CH_4 ($^1A_1$)	−15.8 ± 0.3	−16.0 ± 0.1
C_2H_2 ($^1\Sigma g^+$)	55.6 ± 0.4	56.3 ± 0.2
	(55.1 ± 0.4)[a]	54.3
C_2H_4 ($^1Ag'$)	15.1 ± 0.4	14.6 ± 0.1
C_2H_6 ($^1A_{1g}$)	−15.9 ± 0.4	−16.6 ± 0.0
		−16.3 ± 0.0
C_3H_4 ($^1A_1$) allene	48.1 ± 0.5	47.4 ± 0.3
C_3H_4 ($^1A_1$) cyclopropene	70.5 ± 0.5	68.3 ± 0.6
	(69.9 ± 0.5)[a]	
C_3H_4 ($^1A_1$) propyne	46.5 ± 1.5	46.0 ± 0.2
C_3H_6 ($^1A_1'$) cyclopropane	17.4 ± 1.5	16.8 ± 0.1
C_3H_6 ($^1A'$) propene	8.2 ± 1.5	8.4 ± 0.2
C_3H_8 ($^1A_1$) propane	−20.0 ± 1.6	−19.6 ± 0.1
C_3H_5 ($^2A_2$) allyl	42.7 ± 1.5	42.7 ± 0.5
C_6H_6 ($^1A_{1g}$) benzene	24.7 ± 3	24.0 ± 0.2

[a] Recommended value for ΔH_f(0 K) based on lowering the calculated value by 0.5 kcal/mol as described in the text.

Conclusions

Extended basis set CCSD(T) calculations, with corrections for core/valence correlation, scalar relativistic and higher order correction effects, have been performed on eight hydrocarbons, ranging in size from allene to benzene. The resulting theoretical heats of formation, shown in Table 6, are in generally good agreement with experiment. As noted above, most of the ΣD_0 values are lower than the experimental values by ∼0.5 kcal/mol. Consequently, the predicted heats of formation at 0 K are too high by similar amounts. There are only two compounds whose predicted heats of formation lie outside the 1 kcal/mol error limit, acetylene and cyclopropene. We would recommend a value of 55.1 ± 0.4 kcal/mol for $\Delta H_f(C_2H_2)$ at 0 K based on our calculated value for $\Sigma D_e(C_2H_2)$. In addition, we note that there is likely to be an error in the heat of formation of cyclopropene. Based on our results for the other C_3H_4 isomers, where we predict ΔH_f values at 0 K that are too high by 0.5 and 0.7 kcal/mol, we suggest revising the value of the heat of formation for cyclopropene at 0 K to 69.9 ± 0.5 kcal/mol. We note that the G2, G3, and CBS-Q estimates of ΣD_0(cyclopropene) are all in good agreement with our CCSD(T) result, at 645.3, 645.9, and 644.5 kcal/mol, respectively. Our value for ΔH_f(allyl) supports Roth's[69] recent revision of this important thermochemical number.

In addition to the heats of formation of these small-to-medium sized hydrocarbons, the information compiled for this study also provides us with a singlet−triplet gap prediction for CH_2, a number of considerable experimental and theoretical interest.[70,71] The current UCCSD(T) T_0 value is 9.14 ± 0.05 kcal/mol (8.91

with RCCSD(T)), compared with selected experimental values of 9.02 ± 0.01 kcal/mol[72] and 8.998 ± 0.014 kcal/mol.[73] Our estimate is based on frozen core CBS extrapolations using aVTZ → aV5Z basis sets, a core/valence correction of 0.34 kcal/mol, a scalar relativistic correction of −0.06 kcal/mol, and a higher order correction of −0.20 kcal/mol. The latter value came from CCSDT/VQZ calculations. The ZPE difference (−0.22 kcal/mol) was taken from the experimental work of Jensen and Bunker,[73] which differs substantially from the −0.42 kcal/mol (in terms of the accuracy of the experimental energy difference) predicted by harmonic CCSD(T)/aVQZ frequencies.

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