Coupled Cluster Theory Determination of the Heats of Formation of Combustion-Related Compounds: CO, HCO, CO_2, HCO_2, HOCO, HC(O)OH, and HC(O)OOH

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Coupled cluster theory through quasiperturbative, connected triple excitations was used to obtain optimized structures, harmonic vibrational frequencies, and heats of formation for seven small molecules important to hydrocarbon oxidation. For the three systems possessing reliable experimental heats of formation, the level of agreement between theory and experiment was excellent. To achieve this level of agreement and to simultaneously minimize the theoretical uncertainty, it was necessary to apply large correlation consistent basis sets (through septuple ζ in some cases) followed by a number of small, but nonnegligible, energetic corrections. For CO, $\Delta H_f^0(0\ K) = -27.0 \pm 0.2$ (theory) versus -27.20 ± 0.04 kcal/mol (expt). For CO_2, $\Delta H_f^0(0\ K) = -93.7 \pm 0.2$ (theory) versus -93.97 ± 0.01 kcal/mol (expt). For HC(O)OH (formic acid), $\Delta H_f^0(0\ K) = -88.9 \pm 0.4$ (theory) versus -88.7 ± 0.1 kcal/mol (expt). For HCO, the experimental and theoretical values are in near perfect agreement, with $\Delta H_f^0(0\ K) = 10.4 \pm 0.2$ (theory) versus 10.3 ± 2 kcal/mol (expt), although this may be somewhat fortuitous because the experimental value has a large uncertainty. For *trans*-HOCO, we predict a value of $\Delta H_f^0(0\ K) = -43.9 \pm 0.5$ kcal/mol, compared to the revised photoionization value of $\geq -45.8 \pm 0.7$ kcal/mol. Theory, however, is in good agreement with the possible experimental value of -42.7 ± 0.9 kcal/mol suggested in the same photoionization experimental analysis. For HCO_2, theory predicts a value of $\Delta H_f^0(0\ K) = -29.3 \pm 0.4$ versus -30 ± 3 kcal/mol for a recent negative-ion photoelectron measurement. For HC(O)OOH, in which case no experimental data exists, $\Delta H_f^0(0\ K) = -65.6 \pm 0.6$ kcal/mol. *trans*-HOCO is only slightly bound (1.1 kcal/mol) with respect to the $H + CO_2$ asymptote. HCO_2 is 15.7 kcal/mol higher in energy than *trans*-HOCO and lies above the $H + CO_2$ asymptote by 14.6 kcal/mol. It is only bound with respect to the OH + CO asymptote by 9.0 kcal/mol. Three widely used parametrized methods (G2, G3, and CBS-Q) were compared to the best coupled cluster heats of formation and found to differ by up to 3.2 kcal/mol.

Introduction

The oxidation of hydrocarbons plays a key role in combustion and atmospheric processes. As one moves down through the oxidation cycle, carbon centers lose bonded hydrogens and carbons and gain oxygens. Thus, accurate knowledge of the thermochemistry of molecules possessing a single carbon atom with hydrogen and oxygen atoms as substitutents is key to a better understanding of such oxidation processes. We have already demonstrated an ability to reliably calculate the energies of the CO and HCO species.[1−3] The hydroxy formyl radical, *trans*-HOCO, is important in the oxidation mechanism of CO to CO_2 via the reaction of OH radicals with CO. This reaction helps determine the concentration of OH in the troposphere and is the main source of heat in combustion processes.

There have been extensive experimental[4−23] and theoretical studies[24−32] of the OH + CO reaction involving the *trans*-HOCO intermediate. Despite these studies, there is significant uncertainty about the well depth of *trans*-HOCO relative to the OH + CO asymptote, $\Delta H_{well}(OH + CO)$. The most widely accepted experimental value of the well depth, $\Delta H = 35.4$ kcal/mol, is based on $\Delta H_f^0(trans\text{-HOCO}) = -52.5$ kcal/mol derived from a photoionization measurement.[4,33] However, a recent reinterpretation of the photoionization spectra suggests that $\Delta H_f^0(trans\text{-HOCO}) \geq -45.8 \pm 0.7$ kcal/mol at 0 K (−46.5 kcal/mol at 298 K).[5,34] The new analysis shows that the photoionization threshold is difficult to measure due to very weak threshold transitions. This suggests that HOCO should have a well depth that is no more than 29.4 kcal/mol. A change of this magnitude has significant implications for computational studies of the reaction rate constants and quantum-mechanical scattering calculations using the previous well depth of 35.4 kcal/mol.

There have been a number of theoretical studies of the *trans*-HOCO radical.[34−41] A recent ab initio study[35] using the Gaussian-3 (G3)[42,43] and CBS-QB3[43] parametrized methods reported well depths in the range of 24.9 (G3) to 25.4 (CBS-QB3) kcal/mol. Another recent study[36] at the extrapolated coupled cluster theory level gave $\Delta H_{well}(OH + CO) = 25.34$ kcal/mol at 0 K. The *trans*-HOCO radical has been established to have a $^2A'$ ground state; that is, the unpaired electron lies in the plane of the molecule.

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The HCO_2 radical, the prototypical acyloxyl radical, is an isomer of *trans*-HOCO and can be formed by the loss of H from the OH bond in formic acid [HC(O)OH], by rearrangement, or by the addition of H atoms to the carbon atom in CO_2. HCO_2 has been the subject of a large number of studies, beginning with the early minimal basis set configuration-interaction (CI) work of Baird and Taylor in 1980.[44] The unpaired electron in this radical can occupy one of three nearly degenerate $6a_1$, $4b_2$, or $1a_2$ oxygen lone-pair orbitals, which correspond to the in-phase or out-of-phase nonbonding σ orbitals or the out-of-phase π orbitals, respectively. Beyond the complexity arising from these energetically similar states, this radical displays symmetry breaking at the restricted open-shell Hartree−Fock (ROHF) level of theory. Lower-energy, symmetry-broken solutions of the Hartree−Fock (HF) equation exist at the C_{2v}-symmetric geometries. The σ surface also possesses a Jahn−Teller double cone. Although the energies of the HCO_2 σ states $^2B_2$ and $^2A_1$ and π state $^2A_2$ (C_{2v} symmetry) are expected to be nearly degenerate with respect to both each other and the C_s-symmetry $^2A'$ and $^2A''$ states, their chemistry will differ. The solid-state electronic spin resonance spectra of several acyloxyl radicals have been interpreted in terms of an unsymmetrical spin distribution. In contrast to this, McBride and Merrill found a symmetrical $^2B_2$ spin distribution for the benzoyloxyl radical.[45] Thus, experiment provides no unequivocal guideline as to the nature of the lowest energy state.

Peroxyformic acid [HC(O)OOH] has been the subject of a recent study by Camaioni and Pratt[46] focused on understanding how peroxy acids hydroxylate alkanes via C−H activation. These authors performed density functional theory (DFT) calculations to characterize the transition states and relative energetics for the general reaction $R{-}H + HOOCH{=}O \rightarrow R^\bullet + HOH + OCH{=}O$ (formyloxyl radical), where R = methane, ethane, propane, and isobutene. An accurate determination of the energetics requires accurate heats of formation of both peroxyformic acid and the formyloxyl radical. For R = methane, the authors were able to use a variety of basis sets and levels of theory. DFT with the aVTZ basis set predicts a barrier that is approximately 3 kcal/mol smaller than that of coupled cluster theory through singles and doubles and coupled cluster theory through perturbative triple excitations [CCSD(T)] with the same basis set.

Significant progress has been made in the past decade in developing computational strategies capable of accurately predicting a range of thermochemical properties. The best such strategies have been applied to benchmark collections of 100−200 small and experimentally well-characterized molecules composed of first- through third-period elements. A measure of the success of these methods at reproducing experimental results can be found in a *mean* accuracy of ∼1−3 kcal/mol, which is only slightly larger than the associated experimental uncertainty.

Some of the new approaches rely on embedded parameters (adjusted to improve agreement with experiment) to achieve their success and thereby circumvent the slow convergence of the 1-particle and *n*-particle expansions that characterize electronic-structure methods. Examples of embedded parameter methods include the popular Gaussian-1,[47] Gaussian-2 (G2),[48] and G3[42] family of methods from Pople and co-workers, the complete basis set (CBS) methods of Petersson and co-workers,[49−51] the Weizmann-1 method of Martin and de Oliveira,[52] and the modified G2 method of Fast et al.[53]

An alternative approach, which eschews the empirical parameters in favor of a greatly increased computational expense, is intended to avoid the potential bias introduced by the empirical parameters and to provide a systematic road map to achieving arbitrarily higher accuracy. This approach combines large basis sets and CCSD(T).[54−56] To partially reduce the cost of these calculations, we implicitly assume that a number of small (but nonnegligible) corrections to the energy difference of interest can be computed separately and treated as additive corrections to the raw coupled cluster results. We have applied this approach in a series of recent papers[1−3,57−63] and have shown it to be capable of high accuracy in studies on more than 130 molecules.

In fact, in a recent investigation, we were able to argue that although all major thermochemical tables recommend a value of ΔH_f^0(OH) on the basis of a spectroscopic approach, the correct value is 0.5 kcal/mol lower, consistent with the latest experimental photoionization results.[64,65] The reliability of the theoretical conclusion was bolstered by our ability to reduce the uncertainty in a series of computed heats of formation and ionization energies to <0.2 kcal/mol. The theoretical results were found to be in agreement with three separate experiments (mass-selected photoionization measurements, pulsed-field-ionization photoelectron spectroscopy measurements, and photoelectron−photoion coincidence measurements) utilizing the positive ion cycle to derive the O−H bond energy in water.

As discussed below, corrections to raw frozen-core (FC) coupled cluster atomization energies are required in order to achieve high accuracy. These corrections must account for basis set incompleteness, core/valence (CV) correlation effects, scalar-relativistic effects, and atomic spin−orbit effects. Whenever possible, we also include a correction for the difference between CCSD(T) and full configuration interaction (FCI), which represents the exact solution of the time-independent, nonrelativistic, Born−Oppenheimer Schrödinger equation for a given basis set. However, the factorial growth in the computational cost of FCI with the number of basis functions and electrons makes it intractable for all but the smallest of systems.

Although this composite approach is potentially capable of higher uniform accuracy than the parametrized methods, the substantial increase in the computational cost relative to the parametrized methods currently limits its scope. With the present hardware and software, the composite approach can be applied to molecules containing fewer than 10−15 atoms, including assorted hydrogens. All of the applications of this approach to date have been run on single processors. As parallel hardware and software continue to improve, the maximum affordable system size can be expected to grow. In certain instances, when lower-order correlation treatments, for example, second-order perturbation theory, can be used in place of coupled cluster theory to achieve the requisite accuracy, much larger systems can be accommodated.[66]

The performance of our approach, as measured by its ability to reproduce reliable experimental atomization energies, has been benchmarked with the help of the information on 273 molecules contained in the Environmental and Molecular Sciences Laboratory Computational Results Database.[67] A similar approach, albeit without the compilation of such an extensive database, has been pursued by several other laboratories around the world.[68−74]

In the present work, we apply our composite approach based on CCSD(T)/CBS to determine the heats of formation of seven small organic molecules. The availability of reliable experimental data for CO, CO_2, and HC(O)OH allows them to serve as convenient benchmarks of the accuracy that might be expected for HOCO, HCO_2, and HC(O)OOH, for which no

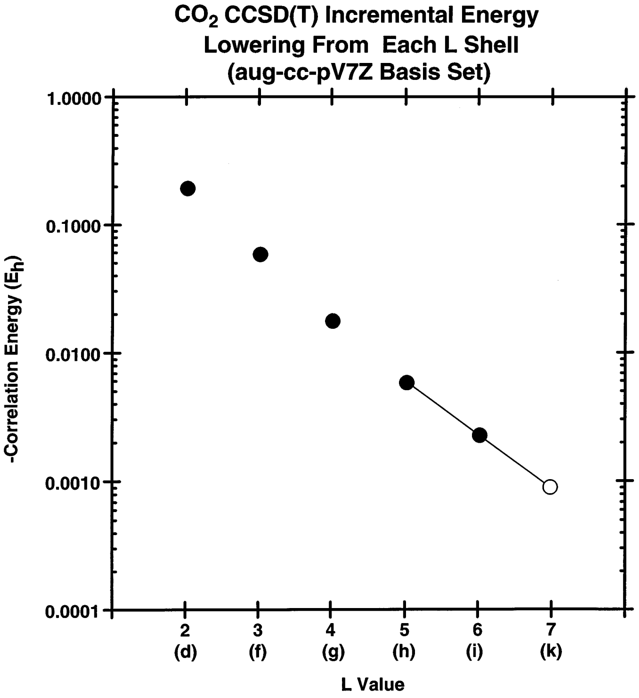

Figure 1. Valence CCSD(T) correlation energy contribution from each angular momentum shell in the aV7Z basis set for CO_2. The contribution from k functions is estimated by an exponential extrapolation of the $l_{max} = 5$ and 6 data points.

reliable experimental measurements are available. We also present new results for HCO, although the experimental data for this molecule is not as reliable.

Methods

1-Particle Basis Set Considerations. The calculations on CO ($^1\Sigma^+$), CO_2 ($^1\Sigma_g{}^+$), and HC(O)OH ($^1A'$) will be used to illustrate certain aspects of our methodological approach, the first of which deals with estimating the CBS limit. Total energies and optimized geometries were obtained from FC coupled cluster calculations that utilized the correlation consistent family of basis sets containing additional diffuse functions. These basis sets are conventionally denoted aug-cc-pVnZ, with $n = D - 7$.[3,75,76] For the sake of brevity, we will abbreviate the notation to aVDZ, aVTZ, etc., throughout the remainder of the text. Only the spherical-component subset (e.g., five-term d functions, seven-term f functions, etc.) of the Cartesian polarization functions was used. All calculations were performed with Gaussian 98[77] and MOLPRO-2000[78] on a single 400-MHz R12000 processor of an SGI Origin 2000. The largest calculation in the current study, in terms of the number of basis functions, required 1.4 days per energy evaluation and involved 711 basis functions.

The largest affordable basis set used in this study was of septuple-ζ quality (i.e., aV7Z). In keeping with the compositional convention of the correlation consistent basis sets, wherein both the number of functions in each angular-momentum shell and l_{max} (the highest angular momentum present in a given basis set) simultaneously increase as the basis set approaches completeness, the aV7Z basis set would be expected to contain k functions ($l_{max} = 7$). Because software limitations prevented us from explicitly including k functions in our calculations, their contribution to the total energy was estimated by performing an exponential extrapolation of the incremental correlation-energy contributions due to h ($l = 5$) and i ($l = 6$) functions. As shown in Figure 1, the convergence of the CO_2 incremental correlation energy is very nearly exponential as a function of l. Moreover, the magnitude of the correlation energy associated with the missing k functions is expected to be small. Similar behavior was observed for CO.

To test the accuracy of this method of approximating the k function contribution, atomic calculations at the configuration interaction singles and doubles (CISD) and CCSD(T) levels of theory using computer codes capable of explicitly handling k functions were performed. These tests suggest that the exponential extrapolation should be accurate to better than 10^{-4} E_h, which is adequate for the current work. Energy *differences* for small molecules, such as CO_2, are likely to benefit from systematic errors in the extrapolation procedure. The extrapolation is expected to yield an estimated accuracy of ±0.02 kcal/mol or better for atomization energies, compared to the results obtained from the explicit inclusion of k functions.

High-accuracy electronic structure calculations impose a heavy computational burden due to the necessity of using large, expensive basis sets. Otherwise, properties may not be sufficiently well-converged with respect to the 1-particle expansion to achieve the desired accuracy. We will ignore the case where a fortuitous cancellation of errors occurs because of the use of small basis sets and low levels of theory, because such combinations typically fail to produce *uniform* accuracy across a wide range of molecules and properties. An example of the need for large basis sets can be seen in diatomic dissociation energies, D_e, where CCSD(T) and small polarized double-ζ basis sets produce results that differ by as much as 20 kcal/mol from the CBS limit. For a fixed basis set size, the basis set truncation error tends to increase with the size of the molecule. Thus, for a system the size of benzene, the error in the VDZ atomization energy, ΣD_e, jumps to nearly 90 kcal/mol.[59] Because of the steep scaling in computational requirements ($\geq N^7$ for N basis functions) associated with highly correlated methods, such as CCSD(T) or multireference configuration interaction (MR-CI), practical considerations currently limit the size of the chemical systems that can be studied with large basis techniques.

As pointed out by Klopper et al.,[79] in order to improve agreement with the CBS limit by an order of magnitude, one must increase the computational load by approximately 4 orders of magnitude. Fortunately, the use of a systematic sequence of basis sets frequently yields properties that converge to the CBS limit in a uniform, monotonic manner. For the total energy, this has led to the use of various extrapolation techniques. Experience has shown that such extrapolations can be remarkably effective in reducing the size of the 1-particle basis set needed to achieve a given level of accuracy.[1,3] In previous work, we based our CBS estimates on one or more of the following formulas: a mixed exponential−Gaussian function of the form[80]

$$E(n) = E_{CBS} + b\exp[-(n-1)] + c\exp[-(n-1)^2] \quad (1)$$

where $n = 2$(aVDZ), 3(aVTZ), or 4(aVQZ); a simple exponential function[81−83]

$$E(n) = E_{CBS} + b\exp(-cx) \quad (2)$$

or one of three formulas that involves the reciprocal of l_{max}[79,84−86]

$$E(n) = E_{CBS} + B/(l_{max} + 0.5)^4 \quad (3a)$$

$$E(n) = E_{CBS} + B/l_{max}{}^3 + C/l_{max}{}^4 \quad (3b)$$

$$E(n) = E_{CBS} + B/l_{max}{}^3 \quad (3c)$$

The latter three formulas should be formally applied to the correlation component of the total energy only, with the HF component extrapolated separately or taken directly from a large basis set value. In practice, the effect on energy differences of treating the HF component separately or extrapolating the total energy is small. Additional extrapolation formulas have also been proposed.[87−92]

Each of the extrapolation formulas is best suited for a particular level of basis set. For example, Truhlar's method is designed for use with the double- and triple-ζ correlation consistent basis sets,[92] whereas eq 1 seems to work best for the observed convergence pattern displayed by the double- through quadruple-ζ basis sets. Finally, eqs 3a−c and similar expressions involving $1/l_{\mathrm{max}}$ are best suited for basis sets beyond quadruple ζ because they are motivated by the $1/Z$ perturbation-theory work of Schwartz, who dealt with two-electron systems in the case where each angular-momentum space was saturated.[93]

The number and variety of the proposed CBS formulas have led to much discussion in the literature over which formula is "best". Several approaches have been followed in trying to answer this question. Some proponents of the $1/l_{\mathrm{max}}$ approach use quintuple- or sextuple-ζ-class basis sets and focus on the agreement between the extrapolated total energies and independent (and presumed accurate) target values, such as those provided by the explicitly correlated CCSD(T)-R12 method.[94] The disadvantage of this approach is that relatively few R12 results are available with the types of large (spdfghi) basis sets needed to obtain converged CCSD(T) energies. The limited number of results suggest an uncertainty of roughly ±0.5 mE_{h} in the CCSD(T) energies with respect to the R12 energies. Furthermore, the use of such large basis sets in the underlying CCSD(T) calculations severely restricts the size of the molecules to which the extrapolation can be applied.

Because absolute accuracy in total energies is seldom the ultimate goal, an alternative approach to determining which formula is best is to focus on one or more energy differences. Figure 2 illustrates several of these factors for CO_2 and HC(O)OH. In the case of CO_2, where the high symmetry ($D_{\infty h}$) permitted calculations up to aV7Z, it is apparent that a basis set of aV6Z quality or better would be required if the *raw* binding energy is to fall within 1 kcal/mol of the apparent CBS limit. The theoretical values in Figure 2 have been adjusted for CV, scalar-relativistic, and atomic spin−orbit effects (see below). The simple exponential extrapolation provides the closest agreement to experiment, by 0.2−0.5 kcal/mol, when aVDZ through aVQZ basis sets are used. If larger sets can be afforded, the $1/l_{\mathrm{max}}$ formula (eq 3a) is best. The experimental heat of formation (and atomization energy) of CO_2 was taken from the JANAF Tables.[33] The experimental heat of formation for formic acid was taken from Pedley et al.[95]

In Table 1, where raw CCSD(T)/aVnZ and extrapolated CBS and atomization energies are shown, the variation in the extrapolated atomization energies as a function of the underlying basis sets for CO and CO_2 is seen to be ≤0.4 kcal/mol. For extrapolations involving the aV5Z or larger basis sets, the variation in CBS ΣD_{e} is reduced by a factor of 2, to 0.2 kcal/mol.

In the case of formic acid (cis), which displays a basis set convergence pattern similar to that of CO_2, the extra two hydrogens and the reduction in molecular symmetry to C_s necessitated a reduction in the size of the largest affordable basis set to aV5Z. For still larger systems, such as peroxyformic acid, aVQZ is the largest affordable basis set. Consequently, in the absence of an effective CBS extrapolation procedure, the best raw atomization energy for peroxyformic acid would be expected to possess a finite basis set error of 4−5 kcal/mol. For formic acid, the simple exponential formula works best for aVDZ through aVQZ basis sets, as it did for CO and CO_2, and the $1/l_{\mathrm{max}}$ formula is superior for larger basis sets. On the basis of these findings, we will adopt eq 2 for estimating the CBS limit of peroxyformic acid and eq 3a for estimating those of the other six molecules. By adopting the CBS extrapolation that provides the apparent best agreement with experiment, we are implicitly assuming that other ignored effects, for example, higher-order correlation effects beyond CCSD(T), are negligible, which, of course, may not be the case.

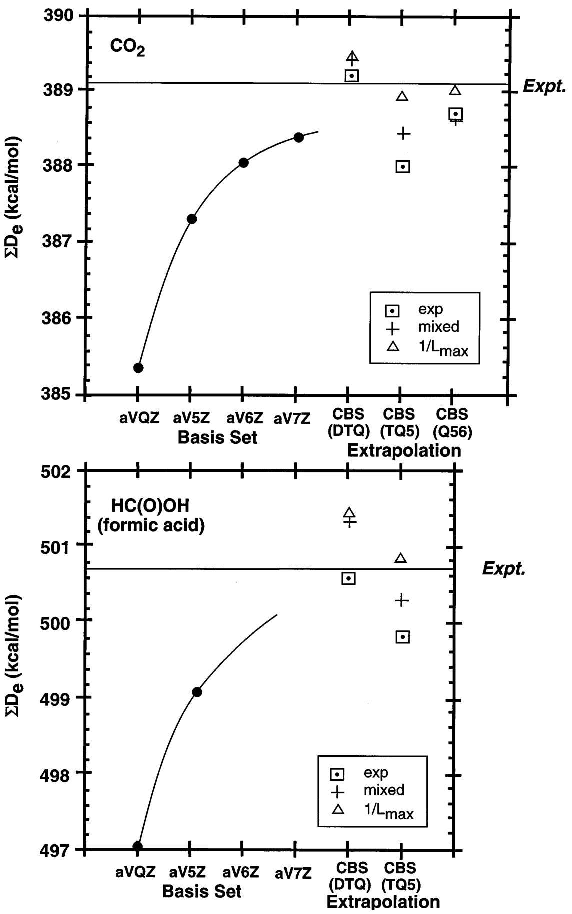

Figure 2. Convergence of the RCCSD(T) electronic atomization energy of CO_2 and HC(O)OH with respect to the level of the 1-particle basis set. The theoretical values have been adjusted for CV correlation effects, molecular scalar-relativistic effects, and atomic spin−orbit effects.

Additional Energetic Considerations. There are three reported coupled cluster approaches to handling open-shell systems. The first is a completely unrestricted method, using unrestricted HF orbitals. The other two approaches begin with ROHF orbitals. One is a completely restricted method, labeled RCCSD(T).[96−99] The other relaxes the spin constraint in the coupled cluster calculation and is sometimes referred to as R/UCCSD(T).[56,100] The latter method is requested in MOLPRO by the keyword "UCCSD(T)" coupled with a restricted open-shell (ROHF) wave function. Dissociation energies were computed with respect to RCCSD(T) atoms in which the symmetry-equivalencing restriction ($p_x = p_y = p_z$) was not imposed. As a check of the sensitivity of the computed atomization energy to the choice of open-shell treatment, ΣD_{e} for *trans*-HOCO was also computed at the R/UCCSD(T) level of theory.

TABLE 1: FC CCSD(T) Total Energies and Electronic (Vibrationless) Atomization Energies from Finite Basis Set Calculations and CBS Extrapolations[a]

basis set	$E_{RCCSD(T)}$	ΣD_e	extrapolation	$E_{RCCSD(T)}$	D_e^{extrap}
CO ($^1\Sigma^+$)					
aVQZ	−113.190 371	256.53	CBS(exp)/aVDTQ[b]	−113.203 61	259.0
aV5Z	−113.199 276	257.74	CBS(l_{max})/aVQ5[c]	−113.206 51	258.7
aV6Z	−113.202 386	258.24	CBS(l_{max})/aV56[d]	−113.205 66	258.8
aV7Z[e]	−113.203 682	258.44	CBS(l_{max})/aV67[f]	−113.205 36	258.7
HCO ($^2A'$)					
aVQZ	−113.720 680	275.58	CBS(exp)/aVDTQ[b]	−113.733 42	277.7
aV5Z	−113.729 654	276.80	CBS(l_{max})/aVQ5[c]	−113.736 94	277.8
aV6Z	−113.732 781	277.32	CBS(l_{max})/aV56[d]	−113.736 07	277.9
CO_2 ($^1\Sigma_g{}^+$)					
aVQZ	−188.389 593	384.72	CBS(exp)/aVDTQ[b]	−188.412 34	388.6
aV5Z	−188.405 172	386.68	CBS(l_{max})/aVQ5[c]	−188.417 82	388.3
aV6Z	−188.410 652	387.54	CBS(l_{max})/aV56[d]	−188.416 41	388.4
aV7Z[e]	−188.412 960	387.83	CBS(l_{max})/aV67[f]	−188.412 96	388.2
HCO_2 ($^2B_2/\sigma$)					
aVQZ	−188.875 152	375.69	CBS(exp)/aVDTQ[b]	−188.896 61	378.8
aV5Z	−188.890 452	377.45	CBS(l_{max})/aVQ5[c]	−188.902 87	379.0
aV6Z	−188.895 801	378.22	CBS(l_{max})/aV56[d]	−188.901 43	379.0
HCO_2 ($^2A'/\sigma$)					
aVQZ	−188.872 224	373.86	CBS(exp)/aVDTQ[b]	−188.893 57	376.8
aV5Z	−188.887 477	375.58	CBS(l_{max})/aVQ5[c]	−188.899 87	377.1
HCO_2 ($^2A_1/\sigma$)					
aVQZ	−188.873 581	374.71	CBS(exp)/aVDTQ[b]	−188.895 28	377.9
aV5Z	−188.888 972	376.52	CBS(l_{max})/aVQ5[c]	−188.901 47	378.1
aV6Z	−188.894 375	377.33	CBS(l_{max})/aV56[d]	−188.900 06	378.2
HCO_2 ($^2A_2/\pi$)					
aVQZ	−188.857 58	364.67	CBS(exp)/aVDTQ[b]	−188.878 70	367.5
aV5Z	−188.872 80	366.37	CBS(l_{max})/aVQ5[c]	−188.885 16	367.8
HOCO (^2A)					
aVQZ	−188.900 224	391.43	CBS(exp)/aVDTQ[b]	−188.922 44	395.0
aV5Z	−188.915 729	393.31	CBS(l_{max})/aVQ5[c]	−188.928 32	394.9
HC(O)OH ($^1A'$)					
aVQZ	−189.567 690	496.55	CBS(exp)/aVDTQ[b]	−189.590 01	500.1
aV5Z	−189.583 510	498.60	CBS(l_{max})/aVQ5[c]	−189.596 36	500.4
HC(O)OOH ($^1A'$)					
aVQZ	−264.623 631	534.83	CBS(exp)/aVDTQ[b]	−264.653 96	538.9

[a] Total energies are given in hartrees (E_h) at the optimized CCSD(T) geometries. Atomization energies are in kcal/mol with respect to RCCSD(T) atoms, in which no orbital symmetry equivalencing was imposed. [b] CBS estimate obtained from the exponential formula (eq 2) using aVDZ, aVTZ, and aVQZ basis set energies. For comparison purposes, the CBS(mix)/aVDTQ formula (eq 1) yields the following atomization energies (kcal/mol): 259.0 (CO), 278.1 (HCO), 388.9 (CO_2), 379.3 (HCO_2; $^2B_2$), 377.2 (HCO_2; $^2A'$), 378.4 (HCO_2; $^2A_1$), 368.0 (HCO_2; $^2A_2$), 395.4 (*trans*-HOCO), 500.8 [HC(O)OH], and 540.0 [HC(O)OOH]. [c] CBS estimate obtained from the $1/l_{max}$ formula (eq 3a) using aVQZ and aV5Z basis set energies. [d] CBS estimate obtained from the $1/l_{max}$ formula (eq 3a) using aV5Z and aV6Z basis set energies. [e] Includes an estimated contribution of k functions (CO = −0.000 50 E_h, CO_2 = −0.000 92 E_h). [f] CBS estimate obtained from the $1/l_{max}$ formula using aV6Z and aV7Z basis set energies.

CV corrections to the atomization energy, ΔE_{CV}, were obtained from all electron CCSD(T) calculations using the correlation consistent cc-pCVQZ basis sets.[101] Experience with even larger CV basis sets suggests that obtaining the CV correction at this level of theory should be accurate to ±0.2 kcal/mol or better.

Two adjustments to ΣD_e are necessary in order to account for relativistic effects. The first correction lowers the sum of the atomic energies (decreasing ΣD_e) by replacing the energies that correspond to an average over the available spin multiplets with the energies for the lowest multiplets. Most electronic-structure codes are only capable of producing average energies. These atomic spin−orbit corrections, ΔE_{SO}, were based on Moore's tables.[102]

A second relativistic correction to the atomization energy was applied to account for molecular scalar-relativistic effects. Because of the expense of four-component correlated calculations for systems containing a dozen or so atoms, more approximate alternatives were adopted. In previous work, we elected to evaluate the scalar-relativistic correction, ΔE_{SR}, using the expectation values of the two dominant terms in the Breit−Pauli Hamiltonian, the so-called mass-velocity and one-electron Darwin (MVD) terms. For this purpose, we used a CISD wave function with a VTZ basis set. Calibration of CISD/VTZ ΔE_{SR} corrections against the limited number of higher accuracy results in the literature at that time led us to conclude that this level of theory should have provided an accuracy of approximately ±0.2 kcal/mol.

For purposes of the present study, we compared the MVD approach and the spin-free, one-electron Douglas−Kroll−Hess (DKH) Hamiltonian method.[103−105] The latter method is presumed to yield more accurate results because the relativistic corrections are bounded from below, unlike the MVD values. Bauschlicher[106] has pointed out that the values from the MVD approach at the CISD/VTZ level of theory can sometimes differ by as much as 0.6 kcal/mol from the DKH values, an unacceptable amount in light of our ±1 kcal/mol target accuracy. The work of Bauschlicher showed that for some systems DKH converges more rapidly with the basis set size, although with sufficiently large basis sets the MVD and DKH results are in good agreement. For the DKH method, ΔE_{SR} was defined as the difference in CCSD(T) atomization energies between the results produced with quadruple-ζ-quality basis sets recontracted for DKH calculations[107] and atomization energies obtained with the normal VQZ basis set. Among the seven molecules examined here, the maximum difference between DKH−CCSD(T) and MVD−CISD was 0.3 kcal/mol. In all cases, the MVD values were larger than the corresponding DKH values. Consequently, we will make use of the DKH values of ΔE_{SR} throughout the remainder of this work.

To convert ΣD_e to $\Sigma D_0{}^0$ and ultimately $\Delta H_f{}^{298}$, we require accurate molecular zero-point vibrational energy corrections, ΔE_{ZPE}. Anharmonic zero-point energies (ZPEs) obtained from experimental or theoretical sources are the preferred choice for this information. We chose the experimental values for CO (3.09 kcal/mol),[108] HCO (8.16 kcal/mol),[109] and CO_2 (7.24 kcal/mol).[110] Although such data is plentiful for diatomic and some triatomic molecules, it is rarely available for systems containing four or more atoms. Nonetheless, for larger systems it may be possible to accurately estimate the anharmonic ZPE.

In our previous studies, we have followed the suggestion of Grev et al.[111] They observed that by simply averaging the ZPEs derived from the theoretical harmonic frequencies, $0.5\Sigma\omega_i$, and experimental fundamentals, $0.5\Sigma\nu_i$, one can obtain an improved estimate of the true ZPE compared to that produced by either set of frequencies alone. However, on purely formal grounds a 3:1 weighting of the harmonic frequencies in the average should be superior to a 1:1 weighting, as can easily be demonstrated for a diatomic molecule. This approximation takes care of all diagonal anharmonicities and is expected to be good to the extent that the computed harmonic frequencies are close to the exact values.

To determine if a 3:1 weighting proved superior in the real-world applications of coupled cluster theory with finite basis sets, we have compared it against the 1:1 weighting for 31 molecules whose anharmonic ZPEs are available from accurate quartic force fields. Of the 31 molecules, 16 are triatomics, and the largest is ethylene, C_2H_4. With the aVDZ basis set, the rootmean-square (RMS) deviation for the 1:1 weighting was smaller than the deviation from the 3:1 weighting, although the difference was only 0.03 kcal/mol. Because CCSD(T)/aVDZ frequencies often deviate by 100−200 cm^{-1} from the more accurate frequencies obtained with the aVTZ or aVQZ basis sets, in a significant number of cases $0.5\Sigma\nu_i$ is closer to the true ZPE than the value obtained from the 1:1 weighting. Despite this, averaging the theoretical and experimental frequencies proved to yield better ZPEs than using either set of frequencies alone, even for the aVDZ basis set. For example, the RMS deviations are 0.32 ($0.5\Sigma\nu_i$), 0.31 ($0.5\Sigma\omega_i$), and 0.22 kcal/mol (1:1 average) with the aVDZ basis set. Increasing the weight of the aVDZ frequencies, as is done with the 3:1 averaging, results in even greater deviation from the true ZPE. For the aVTZ basis set, the two weightings produced essentially identical RMS deviations. Finally, with the aVQZ frequencies, which now agree very well with the exact harmonic frequencies, the 3:1 weighting shows a very slight advantage over the 1:1 weighting. This same pattern can be found for a simple diatomic, such as CO, although the small size of the molecule makes for very small differences in the two weightings (~0.02 kcal/mol). The size of the discrepancy between the two weightings will grow as the size of the ZPE grows.

Unfortunately, given the limitations of our present hardware and software, CCSD(T)/aVDZ frequencies often represent the best available values for medium-size molecules. In the case of HC(O)OOH even, that was prohibitively expensive and we had to resort to second-order Møller−Plesset (MP2) perturbation-theory frequencies. As previously mentioned, we used experimental ZPEs for three of the molecules examined in this study. For three of the four remaining molecules, we estimated the ZPEs by adopting the 1:1 weighting of the theoretical harmonic frequencies and experimental fundamentals. Use of the 3:1 weighting produces ZPEs that are 0.14 (formic acid), 0.06 (*trans*-HOCO), and 0.18 (peroxyformic acid) kcal/mol larger than the 1:1 values. The harmonic frequencies obtained from CCSD(T) and MP2 calculations are given in Table 2, along with the available experimental data.[108,112−115] Because no experimental fundamentals were available for HCO_2, the ZPE was taken as $0.5\Sigma\omega_i$.

There are currently no formal methods for assigning meaningful error bars to the results of ab initio electronic-structure calculations. To associate crude, conservative error bars with our computed atomization energies, we have adopted the spread in the extrapolated values obtained from the mixed (eq 1), exponential (eq 2), and $1/l_{max}$ (eq 3a) formulas. This choice is based on the assumption that in our approach the largest remaining source of error in the theoretical heats of formation for small organic molecules is that arising from the inaccuracies in the CBS estimates. However, in some cases, such as when basis sets of sextuple-ζ quality or better can be used, the leading source of error may shift to the limitations of the CCSD(T) method itself. In several studies, we have examined the effects of higher-order correlation recovery on atomization energies.[58,60,62,65,116,117] These studies involved calculations at the CCSD(T),[118−120] CCSD(TQ), [121,122] CCSD(T)-cf,[123] and FCI levels of theory. Unfortunately, none of the approximate methods were found to produce *uniformly* better agreement with FCI than CCSD(T), although CCSD(T) came closest. When the effectiveness of higher-order correlation methods was calibrated, it was found to be important to use basis sets of at least triple-ζ quality, because smaller sets were found to produce misleading results. The high cost of some of these methods, combined with the *n*! cost of FCI, has hindered progress in this area. Although our choice of assigning error bars on the basis of the spread in the CBS extrapolations ignores potential contributions from the CCSD(T) method itself, it is currently not possible to accurately measure this quantity for polyatomic molecules.

Results and Discussion

Agreement between the experimental and theoretical frequencies in Table 2 is good. For CO, the CCSD(T)/aV5Z value, corrected for CV effects at the pCVQZ basis set level, is within 3 cm^{-1} of the experimental harmonic frequency. For CO_2, the biggest difference resides with the σ_g mode, where theory overestimates experiment by 66 cm^{-1}. The experimental harmonic frequencies were not available for the other molecules. For these systems, theory overestimates the experimental fundamentals by amounts ranging from 2 to 270 cm^{-1}.

To convert $\Sigma D_0{}^0$ to $\Delta H_f{}^0$, we use the standard heats of formation for the elements taken from the NIST/JANAF Tables.[33] To convert from $\Delta H_f{}^0$ to $\Delta H_f{}^{298}$, we employ standard 0 → 298 K temperature corrections taken from either experimental data or computational data where experimental values are not known. The FC CBS dissociation energies are combined with the various corrections already discussed to yield values of ΔH_f(0 K), which are then converted to ΔH_f(298 K) as shown in Table 3. The uncertainties attached to the theoretical values were taken from the spread among the CBS extrapolation equations (1)−(3a). As can be seen, the agreement between theory and experiment for carbon monoxide, carbon dioxide, and formic acid is excellent. As an illustration of the level of accuracy that can be expected from the parametrized methods, the available G2, G3, and CBS-Q heats of formation are also listed in Table 3.

Optimized geometries were obtained for the molecules examined in this study at the FC CCSD(T) level of theory using a threshold of approximately 1.0×10^{-5} E_h/b. These geometries, as well as the available experimental data,[108,124,125] are shown in Figure 3. As an example of the level of agreement between theory and experiment, the aV6Z CO bond length in CO_2 is 1.1619 Å. This compares to the experimental r_e values of 1.1600 and 1.1615 Å.[126,127] The r_0 value in Herzberg's compilation is slightly longer, at 1.1621 Å.[113] CV effects shrink the bond length by 0.0021 Å, bringing the calculated value into near-perfect agreement with the shorter of the two r_e values. The bond lengths in formic acid also agree with their experimental counterparts to within 0.001−0.002 Å.[125] The optimization of the *trans*-HOCO radical at the aug-cc-pV5Z level proved too costly. Consequently, the bond lengths and bond angles in this case were estimated by extrapolating the aug-cc-pVDZ through the aug-cc-pVQZ values using a simple exponential functional form. No experimental structural information is available for this molecule.

CO, CO_2, HCO, and HC(O)OH. Table 3 shows a comparison of the CCSD(T)-based heats of formation and the values predicted by three of the parametrized approaches to the computational thermochemistry. For CO, we are within 0.2 kcal/mol of the experimental value. For CO_2, the differences range from 1.6 (G3) to 3.1 (G2) kcal/mol as compared to our value, which is 0.3 kcal/mol smaller than that of experiment. For formic acid, the differences are smaller, ranging from 0.1 (G3) to 2.0 (CBS-Q) kcal/mol. For HCO, the agreement between our value and the NIST/JANAF value is within 0.1 kcal/mol, and the experimental error bar is ±2 kcal/mol.[33] The NASA/JPL heat of formation at 298 K is only slightly smaller, at 10 ± 1 kcal/mol.[128] For these molecules, the three empirically parametrized methods yield slightly poorer agreement with experi-

TABLE 2: FC Theoretical and Experimental Normal Mode Frequencies (cm^{-1})

CO ($^1\Sigma^+$)

method/basis	σ	method/basis	σ	method/basis	σ
RCCSD(T)/aVDZ	2104.7	RCCSD(T)/aV5Z	2163.5	expt (ω_i)[a]	2169.8
RCCSD(T)/aVTZ	2144.5	RCCSD(T)/aV5Z + CV	2172.7	expt (ν_i)[a]	2163.2
RCCSD(T)/aVQZ	2160.1				

HCO ($^2A'$)

method/basis	a′(bend)	a′(str)	a′(str)	method/basis	a′(bend)	a′(str)	a′(str)
UCCSD(T)/aVDZ	1097.1	1847.9	2676.2	expt (ν_i)[b]	1080.8	1868.2	2434.5
UCCSD(T)/aVTZ	1109.4	1881.6	2703.6				

CO_2 ($^1\Sigma_g^+$)

method/basis	π_u	σ_g	σ_u	method/basis	π_u	σ_g	σ_u
RCCSD(T)/aVDZ	659.0	1317.1	2338.8	expt (ω_i)[c]	674.7	1416.0	2396.2
RCCSD(T)/aVTZ	664.0	1340.9	2373.6	expt (ν_i)[c]	667.4	1388.2	2349.2
RCCSD(T)/aVQZ	664.7	1349.8	2382.0				

HC(O)OH ($^1A'$)

method/basis	a′	a″	a″	a′	a′	a′	a′	a′	a′
RCCSD(T)/aVDZ	616.4	661.5	1034.7	1110.4	1302.2	1390.1	1776.2	3097.2	3723.6
expt (ν_i)[d]	625.0	638.0	1033.0	1105.0	1229.0	1387.0	1770.0	2943.0	3570.0

HCO_2 ($^2B_2$)

method/basis	a_1	b_1	b_2	b_2	a_1	a_1
UCCSD(T)/aVDZ	626.3	991.8	1086.8	1264.8	1440.8	3101.0
CAS/aVDZ[e]	653.2	1022.4	1074.8i	1315.1	1445.5	3187.9
CASPT2/ANO[f]	624	1008	1150	1287	1437	3053
UB3LYP/aCVDZ	647.7	1012.0	1071.4	1271.5	1482.0	3064.2
UB3LYP/aCVTZ	651.2	1023.3	1062.6	1286.2	1492.6	3050.5
MCSCF−CI/DZP[g]	646		961	1314	1477	3197

HCO_2 ($^2A_1$)

method/basis	b_2	a_1	b_1	a_1	b_2	a_1
UCCSD(T)/aVDZ	157.1	640.4	819.2	1150.4	1613.1	2338.7
CAS/aVDZ	869.0i	484.5	803.4	1015.7	1683.1	1714.5
CASPT2/ANO[f]	642	653	830	1153	1669	2392
UB3LYP/aCVDZ	291.4	664.7	840.8	1203.5	1649.2	2331.7
UB3LYP/aCVTZ	239.3	675.0	850.0	1210.2	1657.5	2309.5

HCO_2 ($^2A_2$)

method/basis	b_2	a_1	b_1	a_1	b_2	a_1
UCCSD(T)/aVDZ	660.4	678.8	867.4	1342.6	1373.6	3081.7
RCCSD(T)/aVDZ	1428.0i	677.3	1339.7	1357.8	1446.7	3079.6
MCSCF−CI/DZP[g]	757	696		1372	1437	3177

HCO_2 ($^2A'$)

method/basis	a′	a″	a′	a′	a′	a′
UCCSD(T)/aVDZ	346.2	971.6	1082.5	1263.4	1472.8	3088.0
CASPT2/ANO[f]	331i	958	969	1317	1711	2931
CASSCF/ANO[f]	445	1067	1042	1411	1710	3012

HOCO ($^2A'$)

method/basis	a″	a′	a′	a′	a′	a′
R/UCCSD(T)/aVDZ	523.2	596.5	1036.3	1250.9	1848.0	3781.0
expt (ν_i)[h]	508.1	615	1050.4	1210.4	1852.6	3635.7
expt (ν_i) CO matrix[i]		615	1077	1261	1833	3456

HC(O)OOH ($^1A'$)

method/basis	a′	a′	a″	a′	a′	a″	a′	a′	a′	a′	a′	a′
RMP2/aVDZ	346.8	356.8	489.0	825.4	852.4	1003.8	1141.1	1349.0	1475.5	1747.0	3158.4	3510.2
expt (ν_i)[j]	336.3	331.6	441.3	810	859	999[k]	1125	1340	1442	1744.7	2977	3440.7

[a] Huber and Herzberg, ref 108. [b] Sappey and Crosley, ref 112. [c] Herzberg, ref 113. ω_i are experimentally derived harmonic frequencies. [d] Shimanouchi, ref 114. [e] 13-orbital, 17-electron full conceptual minimal basis set complete active-space calculation. [f] ANO (4s,3p,2d/3s,2p) basis set. Rauk and Armstrong, ref 136. There were 11 orbitals and 13 electrons in the CAS. The oxygen 2s orbitals were excluded from the correlation treatment. [g] McLean et al., ref 135. [h] Jacox, ref 115. Gas-phase values where available; Ne matrix values in other cases. [i] Jacox, ref 115. CO matrix values. [j] Jacox, ref 115. Gas-phase values where available; Ar matrix values in other cases. [k] Estimated value obtained by scaling the MP2 value by 1.011.

TABLE 3: Theoretical and Experimental Enthalpies of Formation

component	ΣD_0 (kcal/mol)	$\Delta H_f{}^0$(0 K)	$\Delta H_f{}^0$(298 K)
CO ($^1\Sigma^+$)			
RCCSD(T)(FC)/CBS(l_{max})[a]	258.7 ± 0.2		
ΔE_{ZPE}[b]	−3.09		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	0.84		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.16		
ΔE_{SO}	−0.30		
total	256.0 ± 0.2	−27.0 ± 0.2	−26.2 ± 0.2
G2[c]	258.0	−29.0	−28.2
G3[d]	256.4	−27.4	−26.6
CBS-Q	256.9	−27.9	−27.1
expt[e]		−27.20 ± 0.04	−26.42 ± 0.04
HCO ($^2A'$)			
RCCSD(T)(FC)/CBS(l_{max})[f]	277.9 ± 0.2		
ΔE_{ZPE}[b]	−8.16		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.05		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.27		
ΔE_{SO}	−0.30		
total	270.2 ± 0.2	10.4 ± 0.2	10.5 ± 0.2
G2[c]	271.3	9.3	9.4
G3[d]	270.9	9.7	9.8
CBS-Q	271.3	9.3	9.4
expt[e]		10.3 ± 2	10.4 ± 2
expt (NASA)[g]		9.9 ± 1	10.0 ± 1
CO_2 ($^1\Sigma_g{}^+$)			
RCCSD(T)(FC)/CBS(l_{max})[a]	388.2 ± 0.2		
ΔE_{ZPE}[b]	−7.2		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.59		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.48		
ΔE_{SO}	−0.52		
total	381.6 ± 0.2	−93.7 ± 0.2	−93.8 ± 0.2
G2[c]	384.6	−96.7	−96.8
G3[d]	383.2	−95.2	−95.3
CBS-Q	384.0	−96.0	−96.1
expt[e]		−93.97 ± 0.01	−94.05 ± 0.01
HC(O)OH ($^1A'$)			
RCCSD(T)(FC)/CBS(l_{max})[h]	500.4 ± 0.4		
ΔE_{ZPE}[i]	−20.7		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.52		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.58		
ΔE_{SO}	−0.52		
total	480.1 ± 0.4	−88.9 ± 0.4	−90.7 ± 0.4
G2[c]	482.0	−90.8	−92.5
G3[d]	480.1	−88.8	−90.6
CBS-Q	481.0	−89.8	−91.6
expt[j]		−88.7 ± 0.1	−90.5 ± 0.4
HCO_2 ($^2B_2$)			
RCCSD(T)(FC)/CBS(l_{max})[f]	379.0 ± 0.4		
ΔE_{ZPE}[k]	−12.2		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.29		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.43		
ΔE_{SO}	−0.52		
total	367.1 ± 0.4	−27.5 ± 0.4	−28.3 ± 0.4
G2	369.5	−29.9	−30.7
G3	368.2	−28.6	−29.4
CBS-Q	369.5	−29.9	−30.7
HCO_2 ($^2A_1$)			
RCCSD(T)(FC)/CBS[f]	378.2 ± 0.4		
ΔE_{ZPE}[k]	−9.6		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.39		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.48		
ΔE_{SO}	−0.52		
total	369.0 ± 0.4	−29.4 ± 0.4	−30.2 ± 0.4
G2	367.4	−27.8	−28.6
G3	370.0	30.4	−31.2
CBS-Q	384.0	−44.4	−45.2
expt[l]		−30 ± 3	−31 ± 3

TABLE 3. (Continued)

component	ΣD_0 (kcal/mol)	ΔH_f^0(0 K)	ΔH_f^0(298 K)
	HOCO ($^2A'$)		
RCCSD(T)(FC)/CBS[h]	394.9 ± 0.5		
ΔE_{ZPE}[i]	−12.8		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.35		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.52		
ΔE_{SO}	−0.52		
total	383.5 ± 0.5	−43.9 ± 0.5	−44.9 ± 0.5
G2	380.8	−45.0	−46.0
G3	383.0	−42.8	−43.8
CBS-Q	384.3	−41.5	−42.5
expt[m]		−52.5 ± 0.6	
expt[n]		≥−45.8 ± 0.7	≥−46.5 ± 0.7
		≥−42.7 ± 0.9	≥−43.4 ± 0.9
	HC(O)OOH ($^1A'$)		
RCCSD(T)(FC)/CBS(exp)[o]	538.9 ± 0.6		
ΔE_{ZPE}[p]	−22.9		
ΔE_{CV} RCCSD(T)/cc-pCVQZ	1.50		
ΔE_{SR} DKH CCCSD(T)/VQZ	−0.67		
ΔE_{SO}	−0.73		
total	516.1 ± 0.6	−65.9 ± 0.6	−68.2 ± 0.6
G2	519.0	−68.8	−71.1
G3	516.6	−66.4	−68.7
CBS-Q	518.7	−68.5	−70.8

[a] CBS extrapolation with the $1/l_{max}$ formula (eq 3a) using the aV6Z and aV7Z basis set energies. The uncertainty is taken from the spread in the exponential, mixed, and $1/l_{max}$ extrapolations. [b] Zero-point vibrational energy is taken from Grev et al., ref 111. [c] Curtiss et al., ref 48. [d] Curtiss et al., ref 42. [e] Experimental heat of formation from ref 33. [f] CBS extrapolation with the $1/l_{max}$ formula using the aV5Z and aV6Z energies. [g] DeMore et al., ref 128. [h] CBS extrapolation with the $1/l_{max}$ formula (eq 3a) using the aVQZ and aV5Z energies. [i] Zero-point vibrational energy is based on $0.5[0.5\Sigma\nu_i(\text{expt}) + 0.5\Sigma\omega_i(\text{CCSD(T)/aVDZ})]$. [j] Experimental heat of formation from Pedley et al., ref 95. [k] Zero-point vibrational energy is based on $0.5\Sigma\omega_i$(UCCSD(T)/aVDZ). [l] Experimental heat of formation for HCO_2 from Kim et al., ref 138. [m] Ruscic et al., ref 4; ref 33. [n] Ruscic and Litorja, ref 5; Francisco, ref 34. [o] CBS extrapolation with the exponential formula using the aVDZ, aVTZ, and aVQZ energies. [p] Zero-point vibrational energy is based on $0.5[0.5\Sigma\nu_i(\text{expt}) + 0.5\Sigma\omega_i(\text{MP2/aVDZ})]$.

ment than the large basis set CCSD(T) approach, although, as stated previously, the latter is much more computationally expensive.

Another approach that has become quite popular because of its low computational cost is DFT with the hybrid B3LYP exchange-correlation functional.[129,130] This method is parametrized to fit a body of experimental thermochemical data through the B3 functional. Although B3LYP is often used with small valence basis sets, such as 6-31G** or 6-311++G**, the method implicitly correlates all electrons, including the core. Thus, to accurately ascertain the B3LYP/CBS limit, it is necessary to partially uncontract the basis sets to reduce basis set contraction error. We have carried out a series of B3LYP calculations on CO_2 and formic acid with the aug-cc-pCVnZ basis sets. For CO_2, the B3YLP/CBS ΣD_e limit compares favorably with the CCSD(T) + CV CBS limit, 388.7 kcal/mol for the former and 389.8 kcal/mol for the latter. However, the 6-31G** and 6-311++G** values are considerably smaller, underestimating the coupled cluster result by as much as 7 kcal/mol. Slightly worse agreement was found for formic acid, where the B3LYP/CBS limit was 2 kcal/mol less than the coupled cluster value, and the small basis set values differed by 9 kcal/mol. Recently, Redfern et al.[131] have pointed out that B3LYP also does poorly for calculations of the heats of formation of the larger *n*-alkanes, yielding errors of approximately 30 kcal/mol with respect to experimental values.

***trans*-HOCO.** The *trans*-HOCO radical is approximately 16 kcal/mol lower in energy than the HCO_2 isomer. It is also ∼2 kcal/mol lower in energy than the cis isomer, with a rotational barrier of ∼8 kcal/mol separating the two minima.[36,38,132] Table 4 contains a summary of previous work on the *trans*-HOCO radical. Most of the calculated ΔH_f(0 K) values cluster within 1−2 kcal/mol about our value of −43.9 kcal/mol, with exceptions for the older Schatz PES result, the raw G2(MP2) result, and the B3PW91 result, which are clearly inaccurate. We note that most of the results in good agreement with our result were not obtained in terms of the raw binding energies converted to ΔH_f but from a variety of reactions based on either the OH + CO asymptote or the H + CO_2 asymptote. The original experimental heat of formation of −52.5 ± 0.6 kcal/mol was obtained from a photoionization measurement.[4,33] This has subsequently been revised to ≥−45.8 ± 0.7 kcal/mol at 0 K on the basis of a reinterpretation of the photoionization threshold behavior. The authors note that this value is an upper limit and that an additional band may be present in the spectra, giving ΔH_f(HOCO) = −42.7 ± 0.9 kcal/mol in good agreement with our value of −43.9 kcal/mol at 0 K. Thus, we agree with the speculation that the ionization energy for HOCO is more likely to be 185.9 ± 0.7 kcal/mol (8.06 ± 0.03 eV) rather than 189.0 ± 0.5 kcal/mol (8.195 ± 0.022 eV).

At the CBS limit, on the basis of aVQZ and aV5Z energies and the $1/l_{max}$ extrapolation, we compute a value of ΔH_{well}(OH + CO) = 25.8 ± 0.5 kcal/mol at 0 K. The largest potential source of error in this value is ΣD_0(HOCO), because D_0(OH) and D_0(CO) agree to within 0.1 kcal/mol with the results obtained from the much larger aV7Z basis set. For the other asymptotic limit, H + CO_2, the HOCO molecule is barely bound. Our calculations predict a value of only 1.1 kcal/mol at 0 K, with an error estimate on the order of 0.3−0.4 kcal/mol. Our calculated value is the most reliable value yet reported and shows that the interpretation of the experimental data, as well as of the scattering calculations, needs to be reinterpreted in terms of the higher heat of formation and consequently smaller well depth.

Figure 3 also shows the optimized geometry of *cis*-HOCO. We find this conformation to be 2.9 kcal/mol higher in energy

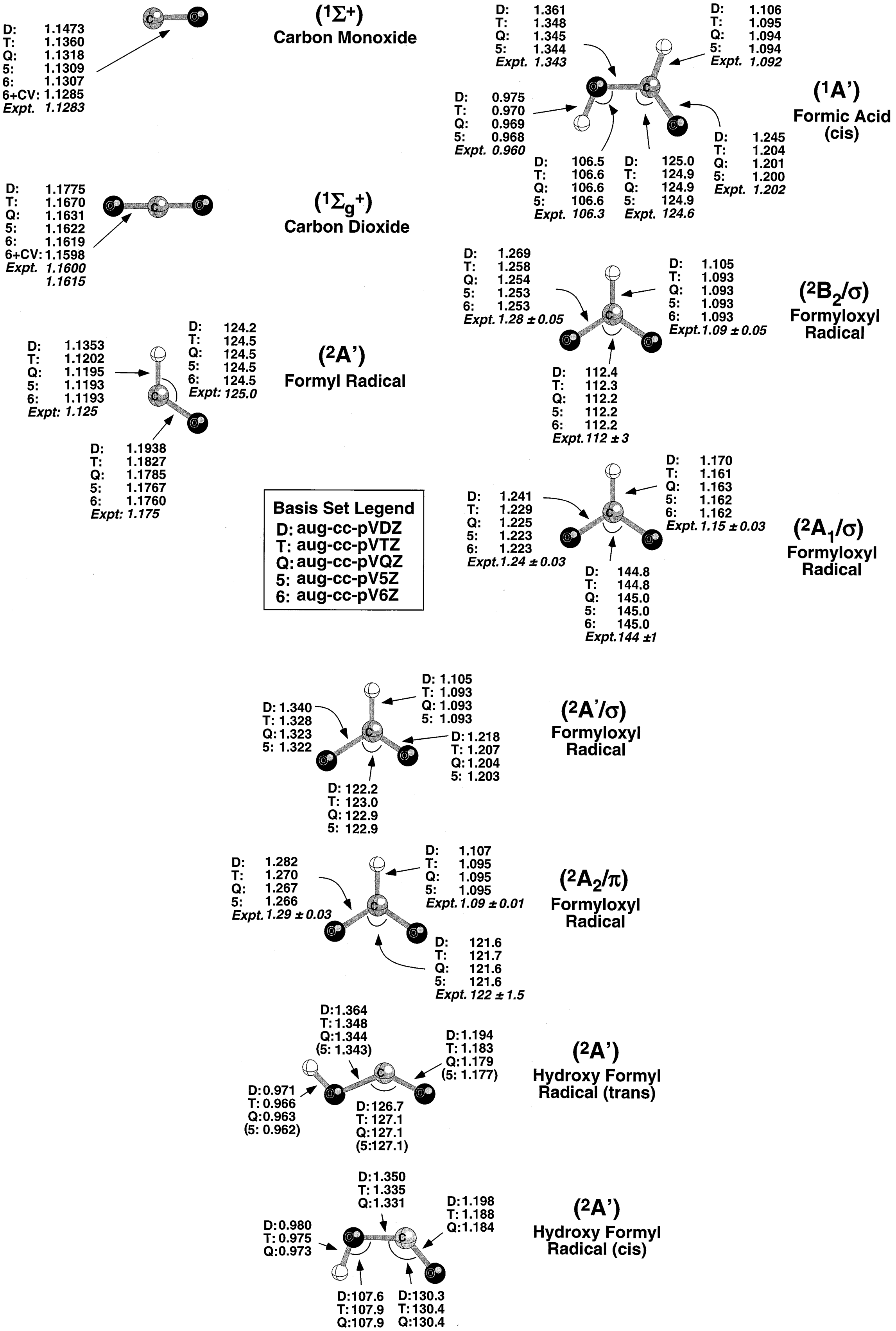

Figure 3. CCSD(T)-optimized and experimental geometries. The aVTZ values for the *trans*-HOCO → *cis*-HOCO transition state were estimated by correcting the CCSD(T)/aVDZ values with the MP2/aVDZ → MP2/aVTZ change in bond lengths and bond angles. The aV5Z values for HOCO were estimated by extrapolating the aVDZ through aVQZ bond lengths and bond angles using a simple exponential fit.

than the trans form, after CBS extrapolation and inclusion of the ZPE, CV, and scalar-relativistic corrections. The trans- → cis-conformer isomerization barrier at the CBS limit is 6.8 kcal/mol (measured with respect to the trans conformer) or 5.8 kcal/mol if ZPEs are included. The latter value is significantly less than the 8.2 kcal/mol obtained by Yu et al.[36]

TABLE 4: Calculated ΔH_f^0 (kcal/mol) for HOCO

method	ΔH_f^0	comment	reference
CBS-QB3	av = −43.8 ± 1.5 (298 K)	based on reactions	35
G3	av = −42.9 ± 1.5 (298 K)	based on reactions	35
CCSD(T)/CBS	−43.7 (0 K)	relative to OH + CO	36
BLYP/aVTZ	−43.7 (0 K)	relative to H + CO_2	39
B3LYP/aVTZ	−45.1 (0 K)	relative to H + CO_2	39
B3PW91/aVTZ	−65.5 (0 K)	relative to H + CO_2	39
B3LYP/6-311++G**	−40.8 (298 K)	relative to H + CO_2	40
MRD-CI/DZP	−40.8 (0 K)	relative to H + CO_2	24
MRD-CI/DZP	−30.7 (0 K)	relative to OH + CO	24
Schatz PES	50.8/−49.8		25
G2(MP2)	−47.8 (298 K)		41
G2(MP2)	−45.4 ± 1.7	isodesmic reaction average	41
CCSD(T)/6-311++G(3df,3pd)	−42.6	$HOCO^+/HOC/H^+ + CO_2$	34

TABLE 5: Previous Theoretical Work on the Energetics of Different States of HCO_2 (kcal/mol)

method	state	min./T.S.	ΔE_{rel}	reference	date
CI/STO-3G	$^2B_2(\sigma)$	T.S.		44	1980
	$^2A'(\sigma)$	min.	0.0		
	$^2A_2(\pi)$	min.	−2.8		
CI/4-31G	$^2B_2(\sigma)$	T.S.			
	$^2A'(\sigma)$	min.	0.0		
	$^2A_2(\pi)$	min.	−1.4		
MRD-CI/DZP + bond	$^2B_2(\sigma)$		0.0	133	1982
	$^2A_1(\sigma)$		7.3		
	$^2A_2(\pi)$		10.0		
MCSCF/SVP	$^2B_2(\sigma)$	T.S.	0.0	134	1983
	$^2A'(\sigma)$	min.	−4.8		
	$^2A_1(\sigma)$	T.S.	6.9		
	$^2A_2(\pi)$	min.	6.2		
	$^2A''(\pi)$	min.	5.4		
	$^2B_1(\pi)$	min	91.4		
MR-CI/DZP	$^2B_2(\sigma)$	T.S.	0.0		
	$^2A'(\sigma)$	min.	2.5		
	$^2A_1(\sigma)$	min.	3.8		
	$^2A_2(\pi)$	min.	5.6		
	$^2B_1(\pi)$	min.	89.7		
MR-CI/TZP	$^2B_2(\sigma)$	min.	0.0	135	1985
	$^2A_2(\pi)$	min.	9.2		
MP4/6-311+G**	$^2B_2(\sigma)$	min.	0.0	136	1994
	$^2A_1(\sigma)$	min.	0.05		
	$^2A'(\sigma)$	min.	3.9		
	$^2A_2(\pi)$	min.	13.5		
QCISD(T)/6-311+G**	$^2B_2(\sigma)$	min.	0.0		
	$^2A_1(\sigma)$	min.	2.3		
	$^2A'(\sigma)$	min.	1.7		
	$^2A_2(\pi)$	min.	10.8		
CASPT2/ANO	$^2B_2(\sigma)$	min.	0.0	137	1995
	$^2A_1(\sigma)$	min.	−1.5		
	$^2A'(\sigma)$	T.S.	4.5		
	$^2A_2(\pi)$	min.	12.6		
MR-CI/ANO	$^2B_2(\sigma)$	min.	0.0		
	$^2A_1(\sigma)$	min.	2.3		
	$^2A'(\sigma)$	min.	2.3		

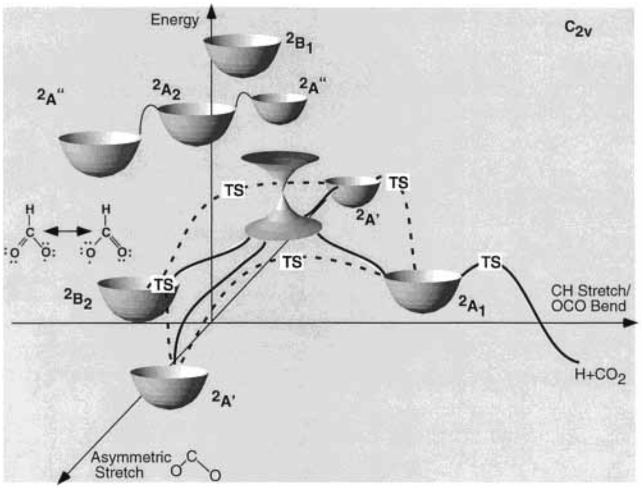

Figure 4. Schematic representation of the HCO_2 low-lying σ and π potential-energy surfaces.

In addition to the RCCSD(T) results shown in Table 1, we have also performed R/UCCSD(T) calculations on HOCO to determine the sensitivity of the atomization energy to the method used in treating open-shell systems. The differences are very small. For example, at the aVQZ basis set level, the difference between the RCCSD(T) and R/UCCSD(T) values is a mere 0.01 kcal/mol.

HCO_2 (Formyloxyl Radical). Table 5 contains a summary of the extensive previous theoretical work on the HCO_2 radical.[44,133−137] Interest in HCO_2 arises from the complexity of the ground- and excited-state surfaces and the additional complication introduced by the symmetry-breaking phenomenon. Not only is the identity of the lowest-energy state very sensitive to the level of theory, but so is the qualitative characterization of the various stationary points. For example, some studies found the $^2B_2$ state to be a transition state (T.S.) connecting the two $^2A'$ asymmetric states, while others found it to be a true minimum (min.). Rauk et al.[136] reported that the $^2A_1$ state was the lowest vibrationless state at the MP2 perturbation level of theory. However, with fourth-order perturbation theory or quadratic CI, the $^2B_2$ state became the lowest. Even the most recent complete active-space second-order perturbation theory (CASPT2) and MR-CI work of Rauk et al.,[137] using an atomic natural orbital (ANO) basis set, found differences in the nature of the $^2A'$ state. The largest basis set used in previous studies of this radical is the [4s3p2d/3s2p] basis set of Rauk et al.[137]

We have applied the same CBS approach to HCO_2 as was used on the other molecules. The optimized geometries, shown in Figure 3, are in good agreement with the experimental structures reported by Kim et al.[138] The energetic results are presented in Table 1. All of the stationary points that were examined were found to be minima by examination of the UCCSD(T) normal modes. UCCSD(T) was used, as opposed to RCCSD(T), to circumvent the effects of symmetry breaking on the ROHF wave functions. No attempt was made to identify the connecting transition states. A schematic representation of the surface is shown in Figure 4. At the CCSD(T) level of theory, the σ surface possesses a complex network of minima and transition states surrounding the Jahn−Teller double cone. The global minimum on the σ surface corresponds to the H + CO_2 products. The CBS(l_{max})/aVQ5 vibrationless-energy ordering (in kcal/mol) is 0.0 ($^2B_2/\sigma$), 0.9 ($^2A_1/\sigma$), 1.9 ($^2A'/\sigma$), 11.1 ($^2A_2/\pi$), and 12.2 ($^2A''/\pi$) in the vicinity of the HCO_2 portion of the potential-energy surface.

As seen in Table 2, the harmonic frequencies and, therefore, the very nature of the stationary points, are sensitive to the level of theory. While the $^2B_2$ state is a local minimum at the CCSD(T), CASPT2, and B3LYP levels of theory, it becomes a transition state with a 13-orbital, 17-electron CAS. CCSD(T), CASPT2, and B3LYP harmonic frequencies yield a zero-point vibrational energy for the $^2B_2$ state that is on the order of 1.8−2.6 kcal/mol larger than the ZPE for the $^2A_1$ state. Because of the long C−H bond distance in the $^2A_1/\sigma$ state, the C−H stretching frequency is much smaller than the corresponding mode in the $^2B_2/\sigma$ state, helping to explain the large difference in the ZPEs for the two states.

Note that the UCCSD(T)/aVDZ normal-mode frequencies for the $^2B_2$ state are similar to the CASPT2 and multiconfiguration self-consistent-field CI (MCSCF-CI) frequencies, suggesting that the UCCSD(T) method should be adequate for predicting the harmonic frequencies for this radical. The impact of symmetry breaking can be clearly seen in the case of the $^2A_2$ state, where UCCSD(T) predicts a lowest-frequency mode of 660.4 cm^{-1} (similar to that of MCSCF-CI), and RCCSD(T) predicts a value of 1428.0i cm^{-1}. The effect of symmetry breaking on the HCO_2 frequencies at the restricted HF and MCSCF levels of theory has been discussed by McLean and Ellinger[37] and by Burton et al.[139]

Because the $^2B_2$ state is only 0.9 kcal/mol lower in energy than the $^2A_1$ state (ignoring ZPEs), when vibrational effects are factored in, the $^2A_1$ state becomes the lowest-energy state at the RCCSD(T) level of theory. This conclusion is, of course, dependent on the accuracy of the ZPEs, which remain problematic despite the application of high levels of theory.

An independent approach to determining the nearly degenerate $^2B_2-^2A_1$ energy difference is via internally contracted CAS-CI. For this purpose, calculations were run with the aVTZ basis set using a reference space consisting of all possible ways of distributing 13 electrons among 11 orbitals. This choice of reference space was obtained from the full conceptual minimal basis set space by excluding the relatively unimportant pair of oxygen 2s orbitals and their four electrons. In the $^2B_2$ symmetry, there are 19 122 reference CSFs, 35.4 million contracted CSFs, and 1.6 billion uncontracted CSFs. The raw $^2B_2$ CAS-CI/aVTZ energy is −188.781 967 E_h, and the $^2B_2-^2A_1$ energy difference is 2.38 kcal/mol, compared to the RCCSD(T) value of 1.23 kcal/mol. After the application of the multireference Davidson and Silver correction,[140] the total energy becomes −188.823 942 E_h (compared to an RCCSD(T) energy of −188.827 272), and the energy difference is 1.92 kcal/mol ($^2B_2$ lower). Thus, the internally contracted CAS-CI results are nearly in quantitative agreement with the results of coupled cluster theory. Of the two estimates, experience suggests that the CCSD(T) value is probably closer to the FCI limit than the CAS-CI value.

By combining the CBS electronic dissociation energy with the corrections previously discussed, we arrive at a value for $HCO_2(^2A_1)$ of $\Delta H_f^0(0\ K) = -29.4 \pm 0.4$ kcal/mol and $\Delta H_f^0(298\ K) = -30.2 \pm 0.4$ kcal/mol. This compares to the value of $\Delta H_f^0(298\ K) = -31 \pm 3$ kcal/mol obtained from photoelectron spectroscopy.[138] The corresponding values for the $^2B_2$ state are $\Delta H_f^0(0\ K) = -27.5 \pm 0.4$ kcal/mol and $\Delta H_f^0(298\ K) = -28.3 \pm 0.4$ kcal/mol.

The G2 and CBS-Q $^2B_2$ $\Delta H_f^0(0\ K)$ values are 2.4 kcal/mol larger in magnitude, whereas the G3 result falls within 1.1 kcal/mol of the CCSD(T) value. The B3LYP/CBS value of ΣD_e is 4.0−4.5 kcal/mol larger than the coupled cluster value corrected for CV effects. Thus, for the molecules studied here, B3LYP/CBS both underestimates and overestimates the best coupled cluster values. If smaller basis sets are used, the errors are much larger, suggesting that B3LYP is not competitive from an accuracy point of view with the much more expensive CCSD(T) approach that we are recommending.

HC(O)OOH. Figure 3 shows the minimum-energy structure of peroxyformic acid, which is stabilized relative to other C_s conformations by the presence of an intramolecular hydrogen bond. The O···H hydrogen-bond distance is 1.897 Å, somewhat shorter than the comparable MP2/aVQZ distance (1.943 Å) in the water dimer.[141] The conformation in which the COOH dihedral angle is trans is 3.2 kcal/mol higher in energy. The conformation in which the OCOO angle is trans is 11.0 higher in energy and corresponds to a transition state.

Following the procedure for computing ΔH outlined above, we arrived at a 0 K heat of −65.9 ± 0.6 kcal/mol. The parametrized methods all yield more negative values, ranging from −66.4 (G3) to −68.8 (CBS-Q) kcal/mol.

Conclusions

Optimized geometries, harmonic vibrational frequencies, and heats of formation were determined for seven small organic molecules relevant to hydrocarbon oxidation. By calibrating our composite theoretical approach in those cases where accurate experimental data was available, we establish the reliability of the method for chemically similar molecules that lack experimental values or for which the experimental values are subject to question. In the present case, the CCSD(T)/CBS-based approach appears capable of predicting bond lengths to within ±0.005 Å, harmonic frequencies to within ±10−20 cm^{-1} (unless symmetry-breaking phenomena are encountered), and heats of formation to within ±0.3 kcal/mol of experimental values for CO, CO_2, HC(O)OH, and HCO. For HCO_2, where the experimental value carries large error bars, the level of agreement is 0.7 kcal/mol.

This level of agreement was accomplished with large basis sets and the application of a series of corrections, dealing with finite basis set effects, CV correlation effects, atomic spin−orbit effects, and molecular scalar-relativistic effects. For the other two molecules, where no experimental heats of formation are available, we predict values of −43.9 ± 0.5 (*trans*-HOCO) and −65.9 ± 0.6 kcal/mol [HC(O)OOH].

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Supporting Information Available: One table listing the FC CCSD(T) total energies and electronic (vibrationless) atomization energies from the aug-cc-pVDZ and aug-cc-pVTZ basis set calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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