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Coupled Cluster Theory and Multireference Configuration Interaction Study of FO, F_2O, FO_2, and FOOF

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Structures, vibrational frequencies, atomization energies at 0 K, and heats of formation at 298 K were obtained for four oxyfluoride molecules, several of which are known to present difficulties for single reference ab initio methods. Whereas much of this work was carried out with coupled cluster theory, multireference configuration interaction calculations were also performed, as an independent check on the reliability of the former. The use of large basis sets (up through augmented sextuple zeta quality in some cases) and a simple basis set extrapolation formula enabled us to accurately estimate the complete basis set limit. However, to achieve near chemical accuracy (±1 kcal/mol) in the thermodynamic properties, it was necessary to include three corrections to the frozen core atomization energies, in addition to the zero-point vibrational energy: (1) a core/valence correction; (2) a Douglas−Kroll−Hess scalar relativistic correction; and (3) a first-order atomic spin−orbit correction. Several approaches to approximating the remaining correlation energy were examined. Theory and experiment are in good agreement for the structures, with the largest difference associated with the FO bond length of FOOF, where the best theoretical value is 0.020 Å shorter than experiment. Agreement with the available experimental heats of formation is good for FO and F_2O and much worse for FOO and FOOF. The final theoretical heats of formation (kcal/mol) at 298 K are 27.9 ± 0.4 (FO), 6.6 ± 0.5 (F_2O), 9.6 ± 0.6 (FO_2), and 9.6 ± 0.9 (FOOF), where the uncertainties include an estimate for the intrinsic errors in the calculations. The corresponding experimental values adopted by the NIST-JANAF tables are 26.1 ± 2.4 (FO), 5.9 ± 0.5 (F_2O), 6.1 ± 0.5 (FO_2), and 4.6 ± 0.5 (FOOF). We suggest that the values reported here for FO and FO_2 are the most reliable values available for these species and recommend their use. For FOOF, the current theoretical as well as that of others differ significantly from experiment and we recommend their use. Our theoretical value for FOOF has the smallest estimated error limits. In light of the demonstrated accuracy of the approach followed here for a large number of molecules and the magnitude of the discrepancy between theory and experiment for FO_2 and FOOF, a reexamination of these systems by experimentalists appears justified.

Introduction

The oxyfluorides constitute an interesting set of molecules to study by computational methods because they contain a large number of nominally inactive lone pairs in terms of Lewis dot structures that can interact with each other at short distances. The four oxygen fluoride molecules FO ($^2\Pi_{3/2}$), F_2O ($^1A_1$), FO_2 ($^2A''$), and FOOF (^1A) have been the focus of a large number of theoretical[1−13] and experimental studies.[14−30] The latter two molecules have proven especially difficult to describe accurately with traditional single reference ab initio methods, such as Hartree−Fock or perturbation theory. A wide range of theoretical approaches has been applied to these molecules, including the complete active space self-consistent field (CASSCF) method, multireference configuration interaction (MR−CI), and coupled cluster theory with singles, doubles, and a quasi-perturbative treatment of connected triple excitations (CCSD(T)).[31−33] More recently, researchers have tested the accuracy of several varieties of density functional theory (DFT). In fact, one of the early successes of DFT in predicting the structures and frequencies of molecules requiring highly correlated methods was FOOF.[34] FOOF is an unusual molecule in that it has a short O−O bond length (1.217 Å), comparable to that in O_2 (1.208 Å), which is 0.26 Å shorter than the bond in the electronically related HOOH. It also has very long O−F bonds (1.575 Å), which are 0.163 Å longer than the O−F bonds in OF_2 (1.412 Å). FOOF is highly reactive. It is a powerful fluorinating reagent which can be used to generate volatile fluorides of actinides, such as U, and has potential use in the processing of nuclear materials.[35−37]

Results obtained from most ab initio single reference methods were found to be in poor agreement with experiment and displayed large variations with respect to the quality of the one-particle basis set. For example, the F−O bond length in FO varies from 1.337 Å at the unrestricted Hartree−Fock (UHF) level of theory with a minimal basis[1] to as much as 2.877 Å with a small polarized basis set.[6] In a series of second-order Møller−Plesset (MP2) perturbation theory calculations, Lee et al.[5] found changes in the F−O bond length of FOOF on the order of 0.2 Å or more accompanying improvements in the basis set. Francisco et al.[8] reported that calculations at the PMP4(SDTQ) level, combined with a basis set that contained multiple sets of polarization functions, produced an F−O bond length in FO_2 that was 0.26 Å shorter than experiment. Coupled with the difficulties in reproducing the experimental geometries has

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TABLE 1: Selected Previous Theoretical ΔH_f^0 (kcal/mol)

system	method	$\Delta H_{f,0}^0$	$\Delta H_{f,298}^0$	ref
FO ($^2\Pi_{3/2}$)	PMP4(SDTQ)(FC)/6-311++G(2df,2p)[a]	27.8 ± 1		Zhao and Francisco[6]
	B3LYP/6-311++G(3df,3pd)	24.31		Ventura and Kieninger[9]
	average of 3 methods[b]	25.4		Ventura and Kieninger[9]
	B3PW91/t-aVQZ	25.2	25.2	Kieninger et al.[12]
	Expt.	25.8± 2.4	26.1± 2.4	NIST-JANAF[40]
F_2O ($^1A_1$)	B3PW91/t-aVQZ	6.2	5.0	Kieninger et al.[12]
	Expt.	6.4 ± 0.5	5.9 ± 0.5	NIST-JANAF[40]
FOO ($^2A''$)	PMP4(SDTQ)(FC)/6-311++G(2d,2p)[c]	22.3 ±3		Francisco et al.[8]
	QCISD(T)(FC)/6-311G(d,p)[d]	8.9 ± 3		Francisco et al.[8]
	B3LYP/6-311++G(3df,3pd)	6.28		Ventura and Kieninger[9]
	average of 3 methods[b]	7.2		Ventura and Kieninger[9]
	B3PW91/t-aVQZ	7.1	6.0	Kieninger et al. [12]
	B3LPY/6-311+G(3df)		4.4	Alcami et al.[13]
	CCSD(T)/6-311+G(3df)		19.0	Alcami et al.[13]
	expt.	6.5 ± 0.5	6.1 ± 0.5	NIST-JANAF[40]
FOOF (^{1}A)	B3LYP/6-311++G(3df,3pd)	8.21		Ventura and Kieninger[9]
	average of 2 methods[b]	8.2		Ventura and Kieninger[9]
	B3PW91/aVQZ	9.0	7.3	Kieninger et al.[12]
	CCSD(T)/ANO[e]	9.7 ± 2.0	8.7 ± 2.0	Lee et al.[11]
	expt.	5.5 ± 0.5	4.6 ± 0.5	NIST-JANAF[40]

[a] Calculated from a combination of an MP4 isodesmic reaction energy and experimental heats of formation for the other species involved in the reaction. [b] Determined as the average value calculated from three (or two) schemes, some of which incorporated experimental heats of formation. [c] Determined as the average value calculated from two isodesmic and isogyric reactions. [d] Determined as the average value calculated from three isodesmic and isogyric reactions. [e] The reported value is based on the isodesmic reaction HOOH + $F_2O \rightarrow H_2O$ + FOOF, using experimental heats of formation for HOOH, F_2O and H_2O.

been the significant difficulties in reproducing the experimental vibrational transitions.

Thermochemical properties, such as heats of formation, ΔH_f^0, have proven especially difficult to reproduce. A summary of reported heats of formation for FO, F_2O, FO_2, and FOOF is shown in Table 1. Agreement between fourth order perturbation theory and a variety of DFT methods for FO and F_2O is good. FO_2 is clearly seen to be the most problematic case, with theoretical values of $\Delta H_{f,0}^0$ ranging from 7.1 up to 22.3 kcal/mol. Only the hybrid DFT methods approach the experimental value. The B3PW91/t-aVQZ value of Kieninger et al.[12] comes within 0.1 kcal/mol of experiment. Alcami et al.[13] found that the B3LYP[38,39] functional produced better agreement with experiment for the heats of formation of five halogen oxides, including FO_2, than did CCSD(T). The most sophisticated study of FOOF was the 1996 work of Lee et al.,[11] who combined CCSD(T) with basis sets ranging from triple-ζ with double polarization up to large atomic natural orbital (ANO) sets, the largest of which was a [5s,4p,3d,2f,1g] contraction. They then used an isodesmic reaction approach to predict ΔH_f(FOOF).

Theory is not alone in finding these molecules challenging. For instance, the NIST-JANAF tables[40] list the $\Delta H_{f,298}^0$ for FOO as 6.1 ± 0.5 kcal/mol, whereas CODATA[41] reports a value of 12 ± 3 kcal/mol. The purpose of the present work is to further calibrate a composite theoretical approach, which attempts to reduce the various sources of error in thermochemical properties to the point where the uncertainty in the answer is on the order of ±1 kcal/mol or better. Besides heats of formation, we will also determine the structures and vibrational frequencies of the four molecules that are the subject of this work. The approach which will be followed has proven capable of high accuracy in more than 150 comparisons with reliable experimental data that were performed with the Environmental and Molecular Sciences Laboratory Computational Results Database.[42−53]

Previous theoretical attempts to determine the heats of formation of FO, F_2O, FO_2, and FOOF have resorted to the use of isodesmic or isogyric reactions. An isodesmic reaction is one in which the reactants and products contain the same number and types of bonds. An isogyric reaction is one in which the number of electron pairs is conserved. By constraining the electronic structure of the reactants and products to be as similar as possible, it is hoped that errors in the theoretical treatment will largely cancel between reactants and products. Experimental heats of formation are used for all species except the one whose value is sought. The approach that we follow does not rely on the use of isodesmic or isogyric reactions in order to compute heats of formation. Because of this, our approach is more general.

Methods

Our composite theoretical approach has been described in detail elsewhere.[45−53] Nonetheless, for the sake of completeness we shall summarize its major steps. We start by addressing the error arising from the use of incomplete one-particle basis sets. This is accomplished through a series of valence CCSD(T) calculations, or some other high-level method, in which the underlying 1-particle basis sets systematically approach the complete basis set (CBS) limit. For this purpose we selected the valence correlation consistent family of basis sets containing additional diffuse functions because of the uniform manner in which they converge to the CBS limit. The diffuse functions allow us to treat systems with highly ionic bonds with as much accuracy as normal covalent bonds. These basis sets are conventionally denoted aug-cc-pVnZ, n = D−6.[54−56] However, for brevity, we abbreviate the names to aVnZ. The largest basis set used was the aV6Z set, which is a (17s,11p,6d,5f,4g,3h,2i) primitive set contracted to [8s,7p,6d,5f,4g,3h,2i]. Only the spherical component subset (e.g., 5-term d functions, 7-term f functions, etc.) of the Cartesian polarization functions are used. All calculations in the present work were performed with Gaussian 98[57] or MOLPRO-2002[58] running serially on an SGI Origin 2000, an IBM Regatta p960 server, or a Hewlett-Packard workstation. The CCSD(T)/aV6Z calculation on FO_2 (567 basis functions in C_s symmetry), which required 13.1 days on a single 400 MHz R12000 processor, was the largest coupled cluster calculation in the present study. Unless otherwise noted, all calculations invoked the frozen core approximation whereby the oxygen and fluorine 1s core electrons were excluded from the correlation treatment.

The FO ($^2\Pi$) bond lengths and harmonic frequencies (discussed below) were obtained from a 7th degree Dunham fit of the potential energy surface.[59] For the other three molecules, geometries were converged to a gradient threshold of approximately 10^{-4} Eh/bohr. An exception to this was the multireference configuration interaction optimization of FOOF with the aVTZ basis set. In this case, a single cycle of quadratic interpolation with step sizes of ±0.005 Å was used because of the time-consuming nature of the calculations. Because neither Gaussian 98 nor MOLPRO possess analytical first derivatives for CCSD(T), a two-point numerical differencing approach was used in obtaining the normal modes.

The majority of our previous thermochemical studies have been performed with the single reference CCSD(T) method, because of its ability to recover a large fraction of the correlation energy when used with large basis sets. Furthermore, whereas the method scales as the 7th power of the number of basis functions, it remains economical enough to allow the use of basis sets of quadruple-ζ quality or better in molecules with 6−7 heavy atoms. As a consequence, we are normally able to estimate the remaining basis set error via simple extrapolation formulas (see below). However, because the molecules examined in this study are thought to present problems for single reference methods, we have also carried out comparable calculations at the MR−CI level of theory. Orbitals for the MR−CI calculations were optimized at the complete active space self-consistent field (CASSCF) level of theory. To reduce the computational load, use was made of the internally contracted, complete active space, multireference configuration interaction (iCAS-CI) method of Werner and Knowles.[60,61] A multireference quadruples correction was applied to the total energy in order to approximately account for higher order correlation effects.[62] Such results are denoted iCAS-CI+Q. Because of the $n!$ scaling of the CASSCF portion of an iCAS-CI+Q calculation and the consequent rapid rise in the number of CI single and double excitations as a function of the basis set size, the use of the method is restricted to relatively small systems.

When computing atomization energies with this method, we employed a "supermolecule" scheme for treating the separated atoms. Internuclear separations were set to 20 Å. At large internuclear distances, the supermolecule approach suffers from a problem associated with mixing of the inner shell core 1s orbitals with the 2s valence orbitals. Although the CASSCF energy is unaffected by the mixing of these orbitals, the CI energy is artificially raised.[63−65] MOLPRO attempts to avoid this problem by resolving the core orbitals. However, in addition, we carried out a two-step CASSCF procedure in which the degenerate orbitals were first constrained to be doubly occupied. This caused the orbitals to be uniquely defined as eigenvectors of a generalized Fock operator. The core orbitals from the first calculation were then frozen and used in a second, full valence CASSCF step. Although the primary goal of this procedure is to obtain correct supermolecule energies, to a lesser extent it also affects energies near the equilibrium geometry.[65] Bond lengths were observed to change by ~0.001 Å and harmonic frequencies by ~0.4 cm^{-1} compared to optimizations performed without the two step procedure.

The electronic configurations of the four molecules under investigation are

$$\mathrm{FO}\ (^2\Pi_{3/2})\ 1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma^2\,1\pi_x^{\,2}\,1\pi_y^{\,2}\,2\pi_x^{\,2}\,2\pi_y^{\,1} \tag{1}$$

$$\mathrm{F_2O}\ (^1A_1)\ 1a_1^{\,2}\,1b_2^{\,2}\,2a_1^{\,2}\,3a_1^{\,2}\,2b_2^{\,2}\,4a_1^{\,2}\,1b_1^{\,2}\,5a_1^{\,2}\,3b_2^{\,2}\,6a_1^{\,2}\,1a_2^{\,2}\,4b_2^{\,2}\,2b_1^{\,2} \tag{2}$$

$$\mathrm{FO_2}\ (^2A'')\ 1a'^2\,2a'^2\,3a'^2\,4a'^2\,5a'^2\,6a'^2\,7a'^2\,1a''^2\,8a'^2\,2a''^2\,9a'^2\,10a'^2\,3a''^1 \tag{3}$$

$$\mathrm{F_2O_2}\ (^1A)\ 1a^2\,1b^2\,2a^2\,2b^2\,3a^2\,3b^2\,4a^2\,5a^2\,6a^2\,5b^2\,7a^2\,6b^2\,7b^2\,8a^2\,9a^2\,8b^2 \tag{4}$$

The iCAS-CI active spaces were taken to be the full valence conceptual minimal basis set space, involving the oxygen and fluorine 2s and 2p orbitals and electrons. The complete active space orbital optimization included all possible excitations among these orbitals. Explicitly, the active spaces and number of configuration state functions (CSFs) are FO (13-el./8-orb., 42 CSFs), F_2O (20-el./12-orb., 480 CSFs), FO_2 (19-el./12-orb., 4,197 CSFs), and FOOF (26-el./16-orb., 47,712 CSFs). For the first three molecules, the entire CAS configuration list was used as the CI reference space, from which all single and double excitations were generated. However, for FOOF, the number of CAS configurations prohibited us from using all of them as the reference space. Instead, we used a subset of the configurations corresponding to all of those with CAS natural orbital (NO) CI expansion coefficients greater than 0.001. This amounted to a reference space of 1312 CSFs. With the aVTZ basis, the number of contracted CI singles and doubles CSFs was 2.0×10^7, corresponding to 2.2×10^9 uncontracted CSFs. Each iCAS-CI+Q/aVTZ calculation for FOOF required approximately 12 h on a single processor of an IBM p690 Regatta system with 1.3 GHZ Power4 processors. Because of the expense of these calculations, they were restricted to the two smallest basis sets (aVDZ and aVTZ). All iCAS-CI+Q calculations were performed with the CAS NOs.

Open shell molecules and atoms were treated with the RCCSD(T) method, which is based on restricted open-shell Hartree−Fock (ROHF) orbitals and imposes a restriction on the coupled cluster amplitudes such that the linear part of the wave function becomes a spin eigenfunction.[66−68] This method is requested in MOLPRO with the keyword "RCCSD(T)". A select few UCCSD(T) calculations, based on UHF orbitals, were also performed with Gaussian 98.

For most polyatomic molecules, it is currently impractical to utilize basis sets that are large enough to reduce the residual basis set truncation error to ±1 kcal/mol when determining energy differences. In an effort to circumvent this problem, the difference between the energy obtained from the largest explicit calculation and the true CBS limit is estimated. For this purpose, a simple formula which expresses the energy as a function of either a basis set index (n) or $1/l_{\max}$, where $l_{\max}$ is the highest angular momentum present in the basis set, is often used. Several such formulas have been proposed.[69−76] Experience has shown that a mixed Gaussian/exponential function performs somewhat better than the $1/l_{\max}$ formulas when the largest affordable basis set is of quadruple-ζ quality.[56] However, when larger basis set results (e.g., aV5Z, aV6Z, etc.) are available, the $1/l_{\max}$ formulas generally produce results in better agreement with experiment.

Because the aV5Z basis set was affordable for all of the molecules under study, we chose to estimate the CBS limit via the following formula:[73]

$$E(l_{\max}) = E_{\mathrm{CBS}} + B/(l_{\max} + 0.5)^4 \qquad (5)$$

In an effort to assess the uncertainty in the CBS estimate, we also made use of a mixed exponential/Gaussian function:[72]

$$E(n) = E_{\mathrm{CBS}} + b\exp[-(n-1)] + c\exp[-(n-1)^2] \qquad (6)$$

where $n = 2$(aVDZ), 3(aVTZ), 4(aVQZ), etc., and a simple exponential function[69−71]

$$E(n) = E_{\mathrm{CBS}} + b\exp(-cx) \qquad (7)$$

In general, the exponential formula does not perform as well as eqs 5 and 6, because the correlation energy dies off more slowly than an exponential. However, in a limited number of cases, it has been shown to produce closer agreement with experimentally derived electronic atomization energies, $\sum D_e$, than either eqs 5 or 6 when used with aVDZ, aVTZ, and aVQZ basis sets.[77] In the present work, we adopt the spread in atomization energies produced by eqs 5−7 as a crude measure of the uncertainty in our couple cluster theory CBS extrapolations.

Normally, absolute accuracy in the total energy is not the foremost goal of an electronic structure calculation. Because thermochemical properties depend on energy differences, it is possible to achieve the requisite accuracy if errors between various chemical systems or along a potential energy curve are balanced. We have demonstrated that the "best" extrapolation formula, as judged by either absolute accuracy in the total energy or the degree of convergence in energy differences, depends on both the molecular system and the quality of the basis sets used in the extrapolation.[49,77] These conclusions are based on calculations through 8-zeta (involving spdfghikl-functions) and comparisons with experiment or other independent estimates of the CBS limit, such as those obtained from explicitly correlated R12 methods.[78]

After estimating the valence CBS limit, several smaller corrections to the electronic energy component are then applied. The largest of these is usually the correction for core/valence (CV) effects, associated with the inclusion of inner shells in the correlation treatment. Our CV calculations for the corrections to the atomization energies were performed with the cc-pCVQZ basis sets of Woon and Dunning[79] at the CCSD(T) level of theory. We have found in a wide range of calculations on neutrals that the diffuse functions in the aug-cc-pVnZ basis sets are not needed in the CV calculations. Next is a correction for scalar relativistic effects, ΔESR, which we obtained from spin-free, one-electron Douglas−Kroll−Hess[80−82] (DKH) CCSD(T) calculations using quadruple-ζ basis sets recontracted for DKH calculations.[83] Finally, a correction is made for atomic spin−orbit effects, ΔE_{SO}. This correction arises from the failure of most electronic structure programs to properly treat the lowest energy multiplet of the dissociated atoms. The atomic spin−orbit corrections, ΔE_{SO}, were based on the tables of Moore,[84] and are as follows (in kcal/mol): −0.39 (F) and −0.22 (O). Because the atomic spin−orbit corrections act to lower the energy of the atomic asymptotes, they result in a decrease of the computed atomization energy. There may also be a spin−orbit correction from open-shell electronic states of the molecule, such as in FO. The CV, scalar relativistic, and atomic spin−orbit corrections are assumed to be additive.

To convert vibrationless atomization energies, $\sum D_e$, to $\sum D_0^0$, and ultimately to heats of formation at 298 K, $\Delta H^0_{\mathrm{f},298}$, we require accurate molecular zero-point vibrational energy corrections, ΔE_{ZPE}. Ideally, we use anharmonic zero-point energies obtained from experimental or theoretical sources. Unfortunately, for polyatomic systems, these are seldom available. In the current study, we estimated the anharmonic zero-point energy by following the suggestion of Grev et al.[85] They observed that by averaging the zero-point energies based on calculated harmonic frequencies, $0.5\Sigma\omega_i$, and experimental fundamentals, $0.5\Sigma\nu_i$, one can obtain a better approximation to the true zero-point energy than with either set of frequencies alone. In a previous study we compared the 1:1 averaging of harmonic and fundamental frequencies for 31 molecules having accurate anharmonic zero-point energies taken from the literature. The root-mean-square errors were 0.23, 0.11, and 0.09 kcal/mol for the aVDZ, aVTZ, and aVQZ basis sets, respectively.[48] We also tested a 3:1 weighting, which should perform better on purely formal grounds providing that very accurate harmonic frequencies are available. When CCSD(T)/aVDZ frequencies were used, the 3:1 weighting produced slightly poorer results than the 1:1 weighting. With CCSD(T)/aVTZ frequencies, the two weightings yielded the same root-mean-square error, and finally, with CCSD(T)/aVQZ frequencies, the 3:1 weighting was slightly better. Unfortunately, for most polyatomic molecules, CCSD(T)/aVQZ frequencies are extremely expensive computationally and because the frequencies are harmonic, calculations at this level do not generally improve the prediction of heats of formation. In the present work, the frequencies for F_2O and FO_2 were calculated at the CCSD(T)/aVTZ level and at the CCSD(T)/aVDZ level for FOOF. This was the level chosen in terms of balancing the computational requirements with the required accuracy.

Having addressed the error arising from the truncation of the one-particle basis set in the manner described above, it is tempting to apply a similar approach to the n-particle expansion. Within the coupled cluster formalism, one could imagine a sequence of calculations, such as CCSD, CCSDT, and CCSDTQ, leading to the full configuration interaction (FCI) result. However, practical considerations currently make that approach prohibitively expensive. We require an approach that can be applied to systems on the order of benzene or even larger in size. Given the $\sim n^{10}$ scaling of CCSDTQ, it is unlikely that the method could be combined with basis sets of at least triple-ζ quality for medium sized chemical systems soon. In addition, to the best of our knowledge, there is no available open shell CCSDTQ code, a capability that is essential for computing atomization energies.

In previous studies, we have compared the CCSD(T),[86] CCSDT, and CCSD(TQ) methods against FCI and experimental results.[44,46,87] In tests involving a variety of first row hydrides, CCSDT provided no significant improvement over CCSD(T). For other diatomic molecules, the performance of CCSDT for dissociation energies was mixed. In the worse case, the inclusion of iterative triples resulted in a change with respect to the CCSD(T) result which was of the opposite sign to the full configuration interaction change. CCSD(TQ) also failed to reliably improving upon CCSD(T), relative to FCI.

More recently we examined the coupled cluster continued fraction, CCSD(T)-cf, approximation of Goodson.[88] Instead of the computationally expensive CCSD, CCSDT, and CCSDTQ sequence of methods, this empirically motivated approach uses Hartree−Fock (HF), CCSD, and CCSD(T) energies with a simple formula for approximating the FCI energy. The success

TABLE 2: Comparison of Electronic Atomization Energies (kcal/mol) at Various Levels of Theory[a]

system	basis	FCI	CCSD(T)[b]	BD(TQ)[c]	CCSD(T)-cf
H_2O ($^1A_1$)	VDZ	209.07	208.76 (0.31)	208.97 (0.10)	209.04 (0.03)
	VTZ/pVDZ[d]	216.29	216.17 (0.12)	216.06 (0.23)	216.62 (−0.33)
C_2 ($^1\Sigma_g^+$)	VDZ	130.83	129.93 (0.90)	129.42 (1.41)	132.29 (−1.46)
CN ($^2\Sigma$)	VDZ	160.14	157.41 (2.73)	158.62 (1.52)	158.17 (1.97)
N_2 ($^1\Sigma_g^+$)	VDZ	201.58	200.10 (1.48)	200.45 (1.13)	200.83 (0.75)
CH_2 ($^3B_1$)	VTZ	186.72	186.67 (0.05)	186.67(0.05)	186.87 (−0.15)
CH2 ($^1A_1$)	VTZ	176.71	176.33 (0.38)	176.47 (0.24)	176.72 (−0.01)
CH ($^2\Pi$)	VTZ	81.64	82.04 (−0.40)	81.54 (0.10)	81.62 (0.02)
	VQZ	83.20	83.03 (0.17)	NA[e]	83.21 (−0.01)
NH ($^3\Sigma^-$)	VTZ	79.35	79.17 (0.18)	NA[e]	79.34(0.01)
	VQZ	81.62	82.44 (−0.82)	82.22 (−0.42)	82.64 (−1.02)

[a] Geometries were as follows: H_2O $r_{OH} = 0.9594$ Å, $\angle HOH = 103.6°$; C_2 $r_{CC} = 1.2707$ Å; N_2 $r_{NN} = 1.1040$ Å; CH_2 ($^3B_1$) $r_{CH} = 1.0784$ Å, $\angle HCH = 133.52°$; CH_2 ($^1A_1$) $r_{CH} = 1.1105$ Å, $\angle HCH = 101.61°$; CH $r_{CH} = 1.1205$ Å; NH $r_{NH} = 1.03963$ Å (VTZ); and $r_{NH} = 1.03775$ Å (VQZ). Values in parentheses are the errors with respect to the FCI value. [b] Open shell systems were treated with the UCCSD(T) method. [c] Open shell systems were treated with the UBD(T) method. [d] The VTZ basis set was used on oxygen and the VDZ basis set was used on the hydrogens. [e] Value unavailable due to a failure of the calculation to converge or to being aborted.

of the method depends on the nature of the molecular system to which it's applied. Goodson grouped his results into two categories, characterized by whether perturbation theory converges monotonically (class A) or not (class B). In our work, we found that for 20 class A chemical systems, the CCSD(T)-cf total energies were always closer to the FCI result than CCSD(T), although sometimes the differences were small. For class B systems, the level of agreement between CCSD(T)-cf and FCI was noticeably worse. In six out of 19 cases, the CCSD(T)-cf energy was further from FCI than CCSD(T). However, it is possible that CCSD(T)-cf energy *differences* represent an improvement over CCSD(T) even for class B molecules.

The calibration of CCSD(T)-cf against FCI electronic atomization energies, $\sum D_e$, involved a set of diatomic molecules, water and methylene (see Table 2). We also examined the Brueckner doubles with perturbative triples and quadruples, BD(TQ), method,[89] another potential candidate for improving the raw coupled cluster result. For CH with the VQZ basis set and NH with the VTZ basis set, the BD(TQ) entries are missing because the calculations either failed to converge or aborted. Overall, the results are mixed. Out of 11 possible comparisons, CCSD(T)-cf showed an improvement over CCSD(T) in seven cases. BD(TQ) showed an improvement in six cases. One way to look for potential issues with the CCSD(T) starting wave function is to examine the T_1 diagnostic.[90] Values of $T_1 > 0.02$ suggest that care should be taken in using the total energies and that a multiconfiguration representation may be important. In the most dramatic case (CN $^2\Sigma$), where the T_1 diagnostic[90] value of 0.054 suggests that the single reference based coupled cluster theory may be having trouble, the improvement over CCSD(T) was 0.8 kcal/mol for CCSD(T)-cf and 1.2 kcal/mol for BD(TQ). On the other hand, for C_2 with a T_1 diagnostic of 0.039, the CCSD(T)-cf and BD(TQ) $\sum D_e$ values are 0.5 to 0.6 kcal/mol *worse* than CCSD(T) and the corrections are of opposite signs. We tentatively conclude that, for those cases where the CCSD(T)-cf and BD(TQ) methods are in approximate agreement, the predicted correction to CCSD(T) may be viewed as a semiquantitative estimate of the FCI correction. However, in cases where the two methods differ, there is insufficient evidence to choose one over the other. Neither method is accurate enough to be used indiscriminately as an approximate FCI correction to CCSD(T).

Results and Discussion

Theoretical geometries are listed in Table 3, along with the relevant experimental data, where available.[14,91−93] Both the coupled cluster and CI bond lengths for FO ($^2\Pi$) are in good agreement with each other and with experiment, despite the fact that the coupled cluster T_1 diagnostic is 0.030, suggestive of potential problems. The leading CI coefficient, corresponding to the Hartree−Fock (HF) configuration, has a value of 0.953, indicating that the FO wave function has little multireference character. Indeed, even the ROHF value of r_{FO} is within 0.04 Å of experiment. After application of a small core/valence correction, the iCAS-CI+Q and CCSD(T) bond lengths are 0.002 and 0.005 Å shorter than experiment, respectively. In general, the CV correction was found to be ≤0.002 Å for all of the molecules. As shown in Table 3, the difference between the iCAS-CI+Q and CCSD(T) F−O bond lengths in FO begins at 0.005 Å and then decreases as a function of basis set size, approaching a value of 0.003 Å in the basis set limit.

To place the relationship between the coupled cluster T_1 diagnostic and the degree of multiconfigurational nature of the FO wave function into perspective, at least as far as the impact on the computed bond lengths is concerned, a comparison involving closed shell system, such as C_2, O_3, and N_2 is helpful. For C_2 ($^1\Sigma g^+$), the iCAS-CI+Q and CCSD(T) bond lengths agree to within 0.001 Å, even though $T_1 = 0.039$ and $c_1(CI) = 0.837$, where $c_1(CI)$ is the CI coefficient of the leading configuration. C_2 has an important second configuration ($...2\sigma_g^2 3\sigma_g^2 1\sigma_u^2$), which enters the CI wave function with an expansion coefficient of 0.32. Similar results are found for O_3 ($^1A_1$), where $T_1 = 0.027$, $c_1(CI) = 0.873$, and the bond lengths differ by only 0.003 Å. For N_2 ($^1\Sigma g^+$), which represents a typical case in which the wave function is dominated by the Hartree−Fock configuration, the bond lengths also agree to ∼0.001 Å, with $T_1 = 0.013$ and $c_1(CI) = 0.940$. Thus, in systems with T_1 values in excess of 0.02, it is, nonetheless, possible to achieve good agreement between single reference coupled cluster theory, explicitly multireference methods, and experiment.

For the closed shell molecule F_2O ($^1A_1$), $T_1 = 0.016$ and $c_1(CI) = 0.916$. Our best coupled cluster F−O bond length, including a CV correction, is slightly shorter than the CCSD(T)/TZ2P value reported by Lee et al.,[11] 1.402 (this work) vs 1.425 Å (Lee et al.), and 0.010 Å shorter than experiment. At the iCAS-CI+Q/aVQZ level of theory, the bond length is only 0.002 Å longer than the coupled cluster value. We can estimate the F−O bond length in the CI large basis set limit by adding the aVQZ CI correction to the CCSD(T)/aV6Z bond length, arriving at a value of $r_{FO} = 1.403$ Å. This result is 0.009 Å shorter than experiment. It should be noted that with the exception of FO, all of the experimental bond lengths in Table 3 correspond to vibrationally averaged quantities.

TABLE 3: Optimized Theoretical and Experimental Geometries (Angstroms and Degrees)[a]

		RCCSD(T)				iCAS-CI+Q			
system	basis set	r_{FO}	r_{OO}	∠FOX[b]	∠FOOF	r_{FO}	r_{OO}	∠FOX[b]	∠FOOF
FO ($^2\Pi_{3/2}$)	aVDZ	1.3781				1.3832			
	aVTZ	1.3599				1.3634			
	aVQZ	1.3533				1.3566			
	aV5Z	1.3517				1.3549			
	aV6Z	1.3510				1.3542			
	aV6Z + CV[c]	1.3492				1.3524			
	expt.[d]	1.3541				1.3541			
F_2O ($^1A_1$)	aVDZ	1.4324		102.7		1.4354		102.7	
	aVTZ	1.4119		103.0		1.4136		103.0	
	aVQZ	1.4057		103.1		1.4073		103.1	
	aV5Z	1.4041		103.0					
	aV6Z	(1.4035)[e]		(103.0)[e]					
	aV6Z +CV[c]	1.4018		103.0		(1.403)[j]		(103.0)[j]	
	expt.[f]	1.412		103.1					
FO_2 ($^2A''$)	aVDZ	1.6871	1.1988	110.7		1.6978	1.2085	110.8	
	aVTZ	1.6378	1.1933	110.9		1.6486	1.2031	111.0	
	aVQZ	1.6327	1.1882	110.9		1.6420	1.1979	111.0	
	aV5Z	1.6298	1.1872	110.9					
	aV6Z	(1.6282)[e]	(1.1870)[e]	(110.9)[g]					
	aV6Z + CV[c]	1.6265	1.1855	110.9		(1.636)[j]	(1.195)[j]	(111.0)[j]	
	expt.[h]	1.649	1.200	111.2					
FOOF (^{1}A)	aVDZ	1.6279	1.2095	109.2	88.7	1.6480	1.2107	(109.2)[k]	(88.7)[k]
	aVTZ	1.5448	1.2340	108.5	87.3	1.5621	1.2300	(108.5)[l]	(87.3)[l]
	aVQZ	1.5390	1.2289	108.6	87.7				
	aV5Z	1.5386	1.2278	(108.6)[m]	(87.7)[m]				
	aV5Z+CV	1.5372	1.2259	108.6	87.7	(1.555)[n]	(1.222)[n]	(108.6)[m]	(87.7)[m]
	expt.[i]	1.575	1.217	109.5	87.5				

[a] Unless otherwise indicated, all calculations were performed within the frozen core approximation. Values of the T_1 diagnostic with the largest basis sets are 0.030 (FO), 0.016 (F_2O), 0.040 (FOO), and 0.027 (FOOF). [b] X = F (F_2O) or O (FO_2). [c] Includes a CCSD(T)/aug-cc-pCVQZ (or CCSD(T)/cc-pCVTZ for F_2O and FO_2) core/valence correction to the bond length. [d] Bond length taken from Hammer et al., ref 91. [e] Estimated from an exponential fit of the aVTZ through aV5Z bond length and bond angle. [f] Pierce et al., ref 92. [g] Value adopted from the CCSD(T)/aV5Z value. [h] Vibrationally averaged structure from C. Yamada and E. Hirota, ref 93. [i] Jackson, ref 14. [j] Estimated iCAS-CI+Q/aV6Z+CV bond length and bond angle based on the RCCSD(T)/aV6Z+CV values plus the RCCSD(T)/aVQZ → iCAS-CI+Q/aVQZ change. [k] Adopted from the CCSD(T)/aVDZ values. [l] Adopted from the CCSD(T)/aVTZ values. [m] Adopted from the CCSD(T)/aVQZ values. [n] Estimated iCAS-CI+Q/aV5Z bond length and bond angle based on the RCCSD(T)/aV5Z values plus the RCCSD(T)/aVTZ → iCAS-CI+Q/aVTZ change.

Unlike FO and F_2O, where the Hartree−Fock geometries are in at least qualitative agreement with structures obtained from higher level methods, for FO_2, the UHF wave function suffers from severe spin contamination and the molecule dissociates to F (^{2}P) + O_2($^3\Sigma_g^-$). Conversely, at the ROHF level of theory, the F−O bond length is more than 0.2 Å shorter than experiment. CCSD(T) recovers a large enough fraction of the correlation energy that both UHF- and ROHF-based approaches compensate to a large degree for the limitations of the single reference description. The T_1 diagnostic (0.040) is the largest of the four molecules under investigation. Full valence CAS calculations predict a structure with a very long F−O bond length, 2.933 Å, and an O−O bond length in close agreement with the CCSD(T) value. The CI coefficient of the HF configuration is 0.87. The $10a'^2 \rightarrow 11a'^2$ double excitation enters the wave function with a coefficient of −0.29 and a second double excitation ($9a'^2 10a'^2 2a''^2 3a''^1 \rightarrow 9a'^1 10a'^2 2a''^1 3a''^2$ simultaneous singles) enters with a coefficient of −0.12. Despite the strong multireference character to the FO_2 wave function, the CCSD(T) and iCAS-CI+Q geometries are quite similar. Using the aVQZ basis set, the F−O bond lengths differ by 0.009 Å and the O−O bond lengths by 0.010 Å. In each case, the CI bond lengths are longer and in closer agreement to experiment. Following the same procedure as used for F_2O, we can estimate the CI large basis set limit by combining CI/aVQZ corrections with the CCSD(T)/aV6Z+CV bond lengths. This procedure yields bond lengths of 1.636 Å (F−O) vs 1.649 Å (expt.) and 1.195 Å (O−O) vs 1.200 Å (expt.).[93] The corresponding errors are −0.013 and −0.005 Å, respectively.

In the case of FOOF, the restricted Hartree−Fock (RHF) level of theory performs very poorly, producing an F−O bond length that is shorter than experiment by more than 0.22 Å and an O−O bond length that is too long by 0.08 Å. Even with coupled cluster theory, the magnitude of the disagreement with experiment is much larger than is typically observed for molecules composed of first row elements, as well as being larger than the deviations observed for the other molecules in this study. The CCSD(T)/aV5Z+CV F−O bond length is 0.038 Å too short, 1.537 Å (CCSD(T)) vs 1.575 Å (expt.), and the O−O bond is 0.009 Å too long, 1.226 Å (CCSD(T)) vs 1.217 Å (expt.). These bond lengths are also 0.028 Å (F−O) and 0.013 Å (O−O) shorter, respectively, than the values reported by Lee et al.[11] with the TZ2P basis set.

The disagreement between theory and experiment for r_{FO} is substantially reduced at the iCAS-CI+Q level of theory. Because of the cost of the calculations, we froze the FOO and FOOF angles at their coupled cluster values. The coefficient of the Hartree−Fock configuration in the CI wave function is 0.857, indicating a strong multireference character. As seen in Table 3, CI calculations with the aVDZ and aVTZ basis sets produce F−O bond lengths 0.017−0.020 Å longer than their CCSD(T) counterparts, bringing theory into better agreement with experiment. The O−O bond length is also shortened, although the change is much smaller (∼0.004 Å). CI geometry optimizations

TABLE 4: Theoretical and Experimental Harmonic Vibrational Frequencies (cm^{-1})

		RCCSD(T)						iCAS-CI+Q		
system	basis	ω						ω		
FO	aVDZ	990.2						971.3		
	aVTZ	1052.9						1038.7		
	aVQZ	1062.6						1049.1		
	aV5Z	1067.1						1054.0		
	aV6Z	1069.0						1056.0		
	AV6Z+CV	1070.7						1057.7		
	expt. ω_e[a]	1053						1053		
	expt.ν[a]	1048						1048		
		a_1	a_1	b_2				a_1	a_1	b_2
F_2O	aVDZ	441.1	791.4	889.5				442.1	785.1	877.7
	aVTZ	465.5	859.0	945.1						
	expt.[b]	461	831	928				461	831	928
		a′	a′	a′				a′	a′	a′
FO_2	aVDZ[c]	369.0	586.8	1543.5				335.0	546.8	1512.2
	aVTZ	400.4	616.5	1522.9						
	expt.[d]	376	579	1487				376	579	1487
		a	a	b	a	b	a			
FOOF	aVDZ	175.1	348.2	445.5	597.4	607.8	1296.1			
	TZ2P[e]	198	368	491	616	657	1111			
	expt.[f]	202	368	466	630	614	1210			

[a] NIST-JANAF Tables, ref 40. [b] Jones et al., ref 94. [c] For comparison purposes, the UCCSD(T)/aVDZ frequencies are 379.8, 581.2, and 1455.4 cm^{-1}. The classification of the modes is a'_1 = FOO bend, a'_2 = FO stretch, a'_3 = OO stretch. [d] Jacox, ref 95. The first and third frequencies are from the gas phase. The second frequency was obtained in an N_2 matrix. [e] Lee et al., ref 5. [f] Gas-phase fundamentals from Kim and Campbell, ref 96, for the first, second, and fourth through sixth frequencies. The value for the third frequency (466 cm^{-1}) is from an O_2 matrix measurement by Spratley et al., ref 28.

with the aVQZ and aV5Z basis sets were intractable. The estimated CI large basis limit, obtained by applying the CI/aVTZ corrections to the CCSD(T)/aV5Z+CV bond lengths, are r_{FO} = 1.555 Å and r_{OO} = 1.222 Å. The corresponding errors with respect to experiment are −0.020 Å (r_{FO}) and −0.005 Å (r_{OO}). The former error remains the largest among the four molecules.

With the exception of the F−O bonds in FO_2 and FOOF, all of the bond lengths in Table 3 are shown to be relatively insensitive to improvements in the basis set. Convergence to ∼0.002 Å is achieved at the aVQZ basis set level. In the two problematic cases, r_{FO} decreases by 0.057 Å (FO_2) and 0.089 Å (FOOF) along the aVDZ → aV5Z sequence of basis sets.

Theoretical harmonic frequencies and experimental fundamentals are listed in Table 4.[28,94−96] Good agreement was found between the two sets of theoretical values and between theory and experiment. For example, the CCSD(T) and iCAS-CI+Q/aV5Z frequencies for FO were within 14 and 3 cm^{-1} of the experimental harmonic frequency (ω_e = 1053 cm^{-1}), respectively.

CCSD(T) normal-mode analyses for F_2O and FO_2 were obtained by using the aVDZ and aVTZ basis sets. Because of the computational cost, iCAS-CI+Q frequencies were limited to the aVDZ basis set. The CCSD(T) frequencies for F_2O fall within 28 cm^{-1} of the experimental fundamentals. The CI frequencies are 1−12 cm^{-1} smaller than their CCSD(T) counterparts. This suggests that in the large basis set limit the CI values may be in slightly better agreement with experiment. For FO_2, we note that UCCSD(T)/aVDZ frequencies, listed in the footnotes to Table 4, are in better agreement than the RCCSD(T) values. However, the UCCSD(T) value of the O−O stretch is smaller than experiment, whereas we expect harmonic frequencies to be larger than the corresponding fundamentals, as is the case with RCCSD(T).

The largest discrepancy between theory and experiment occurs in the O−O stretch for FOOF (theory, 1296.1 vs expt, 1210 cm^{-1}). This mode appears to be very sensitive to the level of theory and the basis set used in calculating the property. For example, with the aVDZ basis set, the CCSD(T) O−O stretch is 495 cm^{-1} smaller than the MP2 value. The current frequencies are similar to the CCSD(T)/TZ2P values of Lee et al.[11] with the exception of the O−O stretch, where our value is larger than experiment by 86 cm^{-1} and the value of Lee et al. is 99 cm^{-1} smaller than experiment. The errors in the FOOF frequencies parallel the errors in the geometry. At the CCSD(T)/aVDZ level of theory, the predicted r_{OO} is shorter than experiment (theory = 1.210 Å vs expt. = 1.217 Å), and the theoretical O−O stretching frequency is higher than experiment. Similarly, r_{FO} is longer than experiment (theory = 1.628 Å vs expt. = 1.575 Å) and the F−O stretching frequencies are smaller than experiment.

Table 5 contains CCSD(T) and iCAS-CI+Q total energies and electronic atomization energies. As expected, the convergence of $\sum D_e$ to our target accuracy of ±1 kcal/mol requires large basis set expansions, even for such small systems. However, the aV5Z and aV6Z basis sets are large enough that for FO, F_2O, and FO_2 the raw (i.e., unextrapolated) results approach within 1 kcal/mol of the extrapolated CBS(l_{max}/56) values. The “56” notation indicates that energies obtained from the aV5Z and aV6Z basis sets were used in the extrapolation. Even for FOOF, the largest of the four systems, the raw aV5Z atomization energy is only 1.06 kcal/mol smaller than the extrapolated CBS value. Thus, in all cases, the $1/l_{max}$ extrapolation predicts CBS limits for $\sum D_e$ that are reassuringly close to the best directly computed values and increases our confidence in the estimates. The spread in values arising from the three extrapolation formulas, eqs 1−3, is correspondingly narrow. We have assigned uncertainties of ±0.1 (FO), ±0.2 (F_2O and FO_2), and ±0.4 kcal/mol (FOOF) arising solely from our CCSD(T)/CBS extrapolations. Another potential source of error is the intrinsic CCSD(T) error relative to FCI, which will be discussed below. Further increasing our confidence in the CBS estimates

TABLE 5: Total Energies (E_h) and Electronic Atomization Energies (kcal/mol)[a]

		RCCSD(T))		iCAS-CI+Q	
system	basis set	energy	ΣD_e	energy	ΣD_e
FO ($^2\Pi_{3/2}$)	aVDZ	−174.542144	41.86	−174.542449	42.51
	aVTZ	−174.684403	49.01	−174.680727	49.01
	aVQZ	−174.728686	50.85	−174.724076	50.73
	aV5Z	−174.743823	51.42	−174.738749	51.13
	aV6Z	−174.749011	51.69	−174.743757	51.47
	CBS(l_{max}/Q5)	−174.75611	51.92	−174.75066	51.47
	CBS(l_{max}/56)	−174.75447	51.97	−174.74902	51.83
F_2O ($^1A_1$)	aVDZ	−274.146715	76.12	−274.141680	76.02
	aVTZ	−274.375116	88.58	−274.375116	86.84
	aVQZ	−274.446150	91.48	−274.430297	89.35
	aV5Z	−274.470542	92.37		
	aV6Z	−274.478938	92.80		
	CBS(l_{max}/Q5)	−274.49035	93.13		
	CBS(l_{max}/56)	−274.48777	93.24		
FO_2 ($^2A''$)	aVDZ	−249.583129	114.34	−249.582453	116.17
	aVTZ	−249.784183	125.03	−249.776005	125.36
	aVQZ	−249.848045	128.93	−249.837735	128.80
	aV5Z	−249.869333	129.92		
	aV6Z	−249.876714	130.42		
	CBS(l_{max}/Q5)	−249.88661	130.79		
	CBS(l_{max}/56)	−249.88448	130.96		
FOOF (^{1}A)	aVDZ	−349.156896	129.28	−349.147175[b]	
	aVTZ	−349.442127	144.03	−349.419013[b]	
	aVQZ	−349.532077	148.58		
	aV5Z	−349.562467	149.79		
	CBS(l_{max}/Q5)	−349.58714	150.85		

[a] Dissociation is with respect to RCCSD(T) atoms. Symmetry equivalencing of the p_x, p_y, and p_z orbitals was not imposed in the atomic calculations. Values of the T_1 diagnostic with the largest basis sets are 0.030 (FO), 0.016 (F_2O), 0.040 (FOO), and 0.027 (FOOF). [b] Unable to calculate an unbiased atomization energy. See text.

is the stability of the extrapolated values when the basis set is enlarged. For FO, F_2O, and FO_2, the CBS(l_{max}/Q5) and CBS(l_{max}/56) estimates differ by ≤0.2 kcal/mol.

In general, iCAS-CI+Q atomization energies possess intrinsic errors, measured with respect to MR−CI calculations that do not involve the internal contraction approximation, of 1−2 kcal/mol for diatomic molecules.[65] Despite this, CI ΣD_e values can serve as a useful, independent check on the reliability of coupled cluster theory in chemical systems possessing large T_1 diagnostic values. In the present situation, the close level of agreement between CCSD(T) and iCAS-CI+Q atomization energies shown in Table 5 provides evidence of the reliability of coupled cluster theory, despite T_1 values greater than 0.02 and significant multiconfiguration character in the wave functions. Because of the use of the reference space selection step in the iCAS-CI+Q calculations for FOOF, we were unable to obtain an unbiased CI atomization energy for that system. The observed differences in ΣD_e between coupled cluster theory and CI is somewhat counterintuitive in that the largest difference is observed for the system with the smallest T_1 value: $\Delta = -0.2$ (FO), −2.0 (F_2O) and −0.1 kcal/mol (FO_2), with the iCAS-CI+Q values being smaller in each case.

Before discussing the heats of formation, we examine the dissociation energies predicted by several additional higher order methods to see if they might shed light on the magnitude of the CCSD(T) and iCAS-CI+Q errors relative to FCI. Results for FO obtained from six different methods are shown in Table 6. All results were obtained with the aVTZ basis set. Because the T_1 diagnostic for this molecule (0.030) is moderately large, it was considered a good candidate for testing higher order corrections to CCSD(T). The UCCSD(T) and RCCSD(T) D_e values are in almost exact agreement, which is often the case when open shell molecules dissociate to open shell atoms. However, when closed shell molecules dissociate to their constituent atoms, the choice of which open shell coupled cluster method should be used in describing the atoms can influence ΣD_e by 0.1−0.2 kcal/mol per atom. Iteratively including the triple excitations via the UCCSDT method produces a 0.33 kcal/mol increase in D_e and improves agreement with experiment. UCCSD(T)-cf predicts an even larger correction of 0.66 kcal/mol. If this were an accurate reflection of the size of the higher order correction for FO, a failure to include it would introduce a significant error in our final atomization energies (and therefore ΔH_f^0). In contrast to UCCSDT and UCCSD(T)-cf, which both predict increases in D_e, UBD(TQ) predicts a −0.41 kcal/mol decrease. An iCAS-CI+Q calculation agrees with UBD(TQ) on the sign of the correction, but not the magnitude, which for iCAS-CI+Q was only −0.16 kcal/mol. Given the lack of consensus on the sign and magnitude of the higher order correction, it is difficult to know which, if any, estimate reflects the true difference between CCSD(T) and FCI.

TABLE 6: AVTZ Estimates of the Dissociation Energy (kcal/mol) of FO[a]

method	D_e	$\Delta_{UCCSD(T)}$[b]
UCCSD(T)	49.07	0.00
UCCSDT	49.40	0.33
RCCSD(T)	49.01	−0.06
UBD(TQ)	48.66	−0.41
iCAS-CI+Q	48.91	−0.16
UCCSD(T)-cf	49.73	0.66
expt.[c]	53.4	

[a] Frozen core calculations performed at the optimal RCCSD(T)/aVTZ bond length (1.3599 Å). For comparison purposes, the valence CCSD(T)/CBS value of D_e is 52.0 kcal/mol. [b] Change with respect to UCCSD(T). [c] Determined using the NIST-JANAF value of $D_0 = 51.55$ kcal/mol and a ZPE = 1.48 kcal/mol. Atomic spin−orbit, molecular scalar relativistic, and core/valence effects have been added to the experimental value in order to improve the consistency of the comparison with these theoretical values.

Theoretical and experimental heats of formation for the four molecules examined in this study are given in Table 7, along with the various components to ΔH_f. The level of agreement with experiment varies widely. For FO, the final theoretical $\Delta H^0_{f,298}$ value (27.9 ± 0.1 kcal/mol) falls within the error bars of both of the experimental values (26.1 ± 2.4 and 26 ± 3 kcal/mol). If either the CCSDT or CCSD(T)-cf higher order corrections are accurate, the agreement would be even better, but as discussed above, the evidence in this regard is too tentative to be used.

In the case of F_2O, the calculated $\Delta H^0_{f,298}$ of 6.7 ± 0.2 kcal/mol lies just outside the error bars of the NIST-JANAF value of 5.9 ± 0.5 kcal/mol but within our target error limit of ±1 kcal/mol. This level of agreement is typical for molecules with small T_1 values ($T_1 = 0.016$). BD(TQ) yields a correction to $\Delta H^0_{f,298}$ of −0.91 kcal/mol, which worsens agreement with experiment. The CCSD(T)-cf correction is of the opposite sign and quite large (2.24 kcal/mol). The inclusion of this correction results in the theoretical value being larger than experiment by 1.4 kcal/mol, whereas the uncorrected CCSD(T) value is only 0.8 kcal/mol larger.

FO_2 is perhaps the most interesting case and the one that presents the most difficulty from a theoretical perspective. The large UHF spin contamination ($S^2 = 1.59$) causes the UCCSD(T) atomization energy to be 3.3 kcal/mol smaller than the RCCSD(T) value, which would lead to a UCCSD(T) $\Delta H^0_{f,298}$ of around 13 kcal/mol. The RCCSD(T) T_1 diagnostic was 0.040, suggesting that caution should be used when considering the

TABLE 7: Theoretical and Experimental Enthalpies of Formation

FO ($^2\Pi_{3/2}$)

component	D_0 (kcal/mol)	$\Delta H^0_{f,0}$	$\Delta H^0_{f,298}$
RCCSD(T)(FC)/CBS(l_{max})[a]	52.0 ± 0.1		
ΔE_{ZPE}[b]	−1.48		
ΔE_{CV} RCCSD(T)/CVQZ	−0.04		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.07		
ΔE_{SO}[c]	−0.33		
total	50.1 ± 0.1	27.6 ± 0.4	27.9 ± 0.4
expt.[d]		25.8± 2.4	26.1± 2.4
expt.[e]			26 ± 3

F_2O ($^1A_1$)

component	$\sum D_0$ (kcal/mol)	$\Delta H^0_{f,0}$	$\Delta H^0_{f,298}$
RCCSD(T)(FC)/CBS(l_{max})[a]	93.2 ± 0.2		
ΔE_{ZPE}[g]	−3.21		
ΔE_{CV} RCCSD(T)/CVQZ	−0.13		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.11		
ΔE_{SO}	−0.99		
total	88.8 ± 0.2	7.1 ± 0.5	6.6 ± 0.5
expt.[d]		6.4 ± 0.5	5.9 ± 0.5

FOO ($^2A''$)

component	$\sum D_0$ (kcal/mol)	$\Delta H^0_{f,0}$	$\Delta H^0_{f,298}$
RCCSD(T)(FC)/CBS(l_{max})[a]	131.0 ± 0.2		
ΔE_{ZPE}[g]	−3.56		
ΔE_{CV} RCCSD(T)/CVQZ	−0.03		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.16		
ΔE_{SO}	−0.82		
total	126.4 ± 0.2	10.0 ± 0.6	9.6 ± 0.6
expt.[d]		6.5 ± 0.5	6.1 ± 0.5
expt.[e]			6 ± 1
expt.[h]			5.5 ± 0.4
expt.[i]			5.8
expt.[j]			5.2
expt.[k]			5.5
expt.[l]			6.2 ± 0.5
expt.[m]			12 ± 3

FOOF (^1A)

component	$\sum D_0$ (kcal/mol)	$\Delta H^0_{f,0}$	$\Delta H^0_{f,298}$
RCCSD(T)(FC)/CBS(l_{max})[f]	150.9 ± 0.4		
ΔE_{ZPE}[g]	−5.0		
ΔE_{CV} RCCSD(T)/CVQZ	−0.16		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.15		
ΔE_{SO}	−1.20		
total	144.4 ± 0.4	10.5 ± 0.9	9.6 ± 0.9
expt.[d]		5.5 ± 0.5	4.6 ± 0.5
expt.[n]		6.8 ± 0.4	5.9 ± 0.4
expt.[n]		5.5 ± 0.4	4.6 ± 0.2
expt.[o]			4.7 ± 0.3

[a] CBS extrapolation with the $1/l_{max}$ formula (eq 3a) using the aV5Z and aV6Z basis set energies. The uncertainty is taken from the spread in the exponential, mixed and $1/l_{max}$ extrapolations. $\Delta H^0_{f,0}(O) = 58.98 \pm 0.02$ kcal/mol; $\Delta H^0_{f,0}(F) = 18.47 \pm 0.07$ kcal/mol. [b] Experimental anharmonic zero-point energy. [c] Consists of a molecular spin−orbit correction of 0.27 kcal/mol and an atomic correction of −0.60 kcal/mol. [d] NIST-JANAF, ref 40. [e] DeMore et al., ref 20. [f] CBS extrapolation with the $1/l_{max}$ formula (eq 3a) using the aVQZ and aV5Z basis set energies. [g] Obtained by averaging the experimental fundamental and CCSD(T)/aVTZ harmonic frequencies for F_2O and FOO and aVDZ frequencies for FOOF. [h] Lyman and Holland, ref 21. [i] Holland et al., ref 22. [j] Shamonima and Kotov, ref 23. [k] Lyman., ref 25. [l] Pagsberg et al., ref 26. [m] CODATA tables, ref 41. [n] Lyman, ref 25. [o] Kirshenbaum et al., ref 24.

results. To put this in perspective, we have previously examined other systems with large T_1 diagnostics and found that agreement with experiment is often quite good.[46] For example, whereas C_2 is clearly a system with a multiconfiguration wave function, the D_e value obtained through a CCSD(T)-based procedure similar to the one followed here is close to several of the published experimental values; theory = 145.7 vs expt. = 145.8 ± 4.6,[97] 144.4 ± 0.9,[40] and 147.8 ± 0.5 kcal/mol.[98] Interestingly, the CCSDT estimate of the higher order correction for C_2 was more than 2.1 kcal/mol and its inclusion *worsened* agreement with experiment. As mentioned previously, CN is another molecule with a large T_1 value (0.054). In this case, the final theoretical heat of formation underestimates experiment by 1−2 kcal/mol. Thus, whereas the T_1 value for FO_2 indicates that there could be problems with the CCSD(T) dissociation energies, we would nonetheless expect the theoretical value to be within several kcal/mol of experiment. In the case of FO_2, CCSD(T) differs significantly from experiment for all but one of the published $\Delta H^0_{f,298}$ values. The FO_2 theoretical value of $\Delta H^0_{f,298} = 9.6 \pm 0.2$ kcal/mol is closer to the CODATA value of 12 ± 3 kcal/mol than the cluster of experimental values in the 5−6 kcal/mol range. CCSD(T)-cf and BD(TQ) estimates of the higher order correction are 1.60 and 2.53 kcal/mol, respectively. Inclusion of the larger of these corrections leads to a $\Delta H^0_{f,298}$ of 8.2 kcal/mol, which is somewhat closer to the cluster of lower experimental values but still considerably outside the experimental error bars. As described above, the validity of either the CCSD(T)-cf or BD(TQ) corrections is questionable. Among previously calculated FO_2 heats of formation, our CCSD(T) value is closest to the QCISD(T) value ($\Delta H^0_{f,0} = 8.9 \pm 3$ kcal/mol) of Francisco et al.[8] Although the CCSD(T) and QCISD(T) methods are quite similar, the close agreement may be fortuitous given the large difference in the basis sets. The CCSD(T)/6-311+G(3df) value of Alcami et al.[13] is nearly twice as large as our value. Only the DFT heats of formation listed in Table 1 are in good agreement with the NIST-JANAF value. Our results strongly suggest that the DFT values and the cluster of experimental values in the 5−6 kcal/mol range are too small.

As discussed previously, coupled cluster theory has difficulty with FOOF because of the multiconfiguration character of its wave function. Although we were unable to determine a CI atomization energy, our experience with the composite CCSD(T)-based approach in over 150 cases, some of which also had multiconfiguration wave functions, leads us to expect that our predicted heat of formation of FOOF ($\Delta H^0_{f,298} = 9.6 \pm 0.4$ kcal/mol) should be accurate to within several kcal/mol. Our value is completely consistent with the CCSD(T)/ANO value of 8.7 ± 2.0 kcal/mol reported by Lee et al. based on isodesmic reactions.[11] However, our value and that of Lee et al. is substantially larger than either of the experimental values listed in Table 6. The NIST-JANAF[40] value (4.6 ± 0.5 kcal/mol at 298 K) is based on the experimental work of Kirshenbaum et al.,[24] who made a calorimetric measurement at 190 K and assumed that the constant volume heat capacities of the reactants (FOOF) and products ($O_2 + F_2$) were equal over the 190−298 K range. Lyman[25] corrected this value for the actual heat capacity difference and arrived at a value of 4.6 ± 0.2 kcal/mol at 298 K, which aside from the error bars is the value adopted by NIST-JANAF. In his report, Lyman also quotes a slightly larger value said to be based on more recent experimental data. For practical (computational time) reasons, we were unable to compute a BD(TQ) higher order correction for FOOF. The BD(TQ) calculations for the smaller F_2O and FO_2 molecules required over 6 days of computer time each. The B3LYP and B3PW91 DFT values of Ventura and Kieninger[9] and Kieninger et al.[12] fall between NIST-JANAF value and our own. For example, at 0 K, the B3PW91/aVQZ result is 1.5 kcal/mol smaller than our result and 3.5 kcal/mol larger than experiment.

Thus, all three large basis set values (the current one, Lee et al.,[11] and Kieninger et al.[12]) are consistent with a heat of formation substantially larger than the NIST-JANAF value. The Gaussian-2 (G2)[99] and Gaussian-3 (G3)[100] composite methods, which are based on a combination of ab initio calculations and empirical corrections, predict heats of formation of 8.6 and 10.4 kcal/mol, respectively, both substantially larger than the NIST-JANAF value. The G3 value is within 0.1 kcal/mol of our recommended value. The CBS-Q[101] method of Petersson and co-workers is another composite method that is designed to produce reliable thermochemical properties. It predicts a heat of formation of 6.2 kcal/mol, in good agreement with NIST-JANAF, but at odds with all of the other theoretical methods discussed so far.

It is interesting to note that the computed value for the F$-$OOF bond energy at 0 K is 18.0 kcal/mol, compared to the NIST-JANAF experimental value of 19.5 kcal/mol. Thus, the calculated and experimental bond energies differ by less than do the heats of formation of FOOF and FO_2. The calculated heats of formation for FO_2 and FOOF indicate that the two values are within 0.5 kcal/mol of each other at 0 K and essentially identical at 298 K. We estimate the size of additional errors based on errors in zero-point energies, higher order correlation corrections, and other corrections such as core-valence and relativistic to be on the order of ±0.3 kcal/mol for FO and F_2O, ±0.4 kcal/mol for FO_2, and ±0.5 kcal/mol for FOOF. Based on the calculated heats of formation and in contrast to the experimental values, we recommend that the heat of formation of FO at 0 K be revised to a more positive value of 27.6 ± 0.4 kcal/mol. For F_2O, the experimental value appears to be good. For FO_2, we recommend that the value for $\Delta H^0_{f,0}$ be revised to a more positive value of 10.0 ± 0.6 kcal/mol. Finally, for FOOF we recommend a similar upward revision of $\Delta H^0_{f,0}$ to 10.5 ± 0.9 kcal/mol.

Conclusion

Large basis set coupled cluster and configuration interaction calculations were used to determine the structures, harmonic vibrational frequencies, and heats of formation of the four simplest oxyfluoride molecules. Theoretical bond lengths were in reasonable overall agreement with experiment. The largest discrepancy was found in the FO bond length of FOOF, where the best theoretical value is 0.020 Å shorter than experiment. Agreement between theory and experiment is also good for the vibrational frequencies. However, the situation with regard to heats of formation is less satisfactory. Whereas the level of agreement between theory and experiment is good for FO and F_2O, it is much worse for FO_2 and FOOF. The large value of the T_1 diagnostic indicated that the calculated results from coupled cluster theory for FO_2 may not be as reliable as one expects for molecules with smaller values of T_1, but the closeness of the iCAS-CI+Q and CCSD(T) results does not support this contention.

In an effort to account for higher order correlation effects, we examined the reliability of two approaches, CCSD(T)-cf and BD(TQ), against full CI results for some diatomics, water, and CH_2. Neither method proved able to consistently predict the sign and magnitude of the correction needed to bring CCSD(T) into better agreement with FCI. The absence of a reliable and practical higher order correction ultimately limits the accuracy of our predictions and is especially noticeable in cases where single reference coupled cluster theory may be breaking down.

In light of the magnitude of the discrepancy between theory and experiment, the performance of our composite CCSD(T)-based approach for other molecules with large T_1 values, the good agreement with multireference CI results, and its demonstrated accuracy in a large number of cases, we suggest a revision in the heat of formation of FO_2. In the case of FOOF, theory and experiment differ by 5.0 kcal/mol, which is well outside the normal range. Unless FOOF represents a pathological case where coupled cluster theory fails despite a general lack of evidence in from iCAS-CI results in related molecules, we feel that our theoretical value is the more accurate than the experimental values and thus recommend a revision in its heat of formation. We note that handling these materials is quite difficult and therefore suggest that the original calorimetric measurement[24] made in 1959 of the decomposition of FOOF into F_2 and O_2 be reinvestigated. We note that our value for FOOF is consistent with the value of Lee et al. based on isodesmic reactions.[90] In addition, the heat of formation of FOO was determined from kinetic measurements[21−23,25,26] on the reaction of F + O_2, a difficult system to deal with experimentally, and it too should be reexamined.

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