Post-CCSD(T) ab Initio Thermochemistry of Halogen Oxides and Related Hydrides XOX, XOOX, HOX, XO_n, and HXO_n (X = F, Cl), and Evaluation of DFT Methods for These Systems[†]

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Benchmark-quality W4 (and related) thermochemical data were obtained for the fluorine and chlorine oxides and some related hydrides, all of which are of interest for computational modeling of atmospheric processes. Our best available estimates for total atomization energies at 0 K are the following: HO_2 165.97 ± 0.14, H_2O_2 252.08 ± 0.14, HOF 149.24 ± 0.14, FO 51.17 ± 0.10, F_2O 89.43 ± 0.14, FO_2 130.15 ± 0.16, F_2O_2 146.00 ± 0.16, ClO 63.40 ± 0.10, HOCl 156.73 ± 0.14, Cl_2O 96.93 ± 0.16, OClO 122.33 ± 0.16, ClOO 121.88 ± 0.32, Cl_2O_2 142.9 ± 0.3, ClO_3 159.9 ± 0.4, $HClO_2$ 192.0 ± 0.4, $HClO_3$ 258.1 ± 0.3, and $HClO_4$ 313.4 ± 1 kcal/mol. For several of these species, the total atomization energy contains unusually large components from correlation effects beyond CCSD(T). The geometry of FOOF is significantly affected by connected quadruple excitations. A large variety of DFT exchange-correlation functionals have been evaluated for these systems and observations on their performance are offered. Our best available estimates for $\Delta H^{\circ}_{f,0}$ are the following: HO_2 3.65 ± 0.14, H_2O_2 −30.82 ± 0.14, HOF −20.15 ± 0.14, FO 26.28 ± 0.11, F_2O 6.48 ± 0.14, FO_2 6.30 ± 0.16, F_2O_2 8.90 ± 0.18, ClO 24.19 ± 0.10, HOCl −17.51 ± 0.14, Cl_2O 19.24 ± 0.16, OClO 24.26 ± 0.16, ClOO 24.69 ± 0.16, Cl_2O_2 32.3 ± 0.3, ClO_3 45.7 ± 0.4, $HClO_2$ 6.2 ± 0.4, $HClO_3$ −0.9 ± 0.3, and $HClO_4$ 2.9 ± 1.0 kcal/mol. (The corresponding values at 298.15 K are 2.96 ± 0.14, −32.24 ± 0.14, −20.84 ± 0.14, 26.43 ± 0.11, 5.94 ± 0.14, 5.87 ± 0.16, 7.84 ± 0.18, 24.18 ± 0.10, −18.20 ± 0.14, 18.82 ± 0.16, 23.67 ± 0.16, 24.30 ± 0.16, 31.5 ± 0.3, 44.3 ± 0.4, 5.0 ± 0.4, −2.6 ± 0.3, and −0.1 ± 1.0 kcal/mol, respectively.)

I. Introduction

Chlorine oxides are key intermediates involved in the catalytic destruction of ozone.[1] Several ozone depletion theories[2] have been established and the current understanding is that chlorine and bromine oxides are largely responsible for the annual "ozone hole" phenomenon. The lightest halogen, fluorine, is believed to be playing a minor role[3] in ozone destruction, attributed mainly to reactions with tropospheric methane.[4] Fluorine reacts rapidly with methane, compared to ozone, and ends up as hydrogen fluoride, a reservoir species. Models[5] also suggest that less than about two ozone molecules are destroyed per fluorine atom released into the stratosphere. For Cl atoms, this number is 3 to 4 orders of magnitude larger. Similarly, on the atom-for-atom basis, Br is 1−2 orders of magnitude as effective as Cl in destroying ozone due to rapid photolysis of its reservoir species, HBr and $BrONO_2$.[6] This has driven international regulatory agencies to recommend the use of hydrochlorofluorocarbons (HCFCs) as well as hydrofluorocarbons (HFCs) and to phase out the use of Freons. With increased usage of fluorinated compounds, atmospheric measurements[7] have confirmed that both total fluorine in the stratosphere and tropospheric HF are increasing faster than HCl.[8] In this scenario, even if fluorine plays a minor role in ozone depletion, it should not be neglected, and accurate thermochemical data are required for modeling fluorine compounds in atmospheric models. (We note that one of us, J.M.L.M., is part of a IUPAC task group on thermochemistry of radicals and combustion intermediates.[9])

From the chemical point of view, fluorine and chlorine oxides represent an intriguing class of main-group inorganic molecules containing a covalent bond between highly electronegative atoms. Furthermore, they have a large number of unpaired electrons, resulting in strong lone pair−lone pair repulsions. The O−F and O−Cl bonds represent a notorious challenge for single reference electron correlation methods as these species are usually dominated by severe nondynamical correlation (NDC) effects. Notwithstanding, most coupled-cluster studies[10−18] of O_mX_n (X = F, Cl, $m + n \geq 3$) so far assumed that these molecules are adequately described by what has been termed the "gold standard of quantum chemistry", the coupled cluster singles and doubles model with a quasiperturbative triples correction, CCSD(T),[19] together with a large one-particle basis set.

In the present study we apply the recently developed W4 and post-W4 theories to $H_lO_mX_n$ (X = F, Cl) species which are of importance in atmospheric chemistry. W4 theory has been highly successful in treating systems that are dominated by severe NDC effects such as the ozone[20] and boron nitride[21] molecules. We show that post-CCSD(T) contributions have chemically significant effects (ranging between 0.5 and 3.5 kcal/mol for the oxygen halide systems).

Finally, the performance of a variety of DFT exchange-correlation functionals for the halogen oxides is considered.

II. Computational Methods

The self-consistent field (SCF), ROCCSD and ROCCSD(T) calculations[19] were carried out with version 2006.1 of the Molpro program system.[22] All single-point post-CCSD(T)

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calculations were carried out with an OpenMP-parallel version of Mihály Kállay's general coupled cluster code MRCC[23] interfaced to the Austin−Mainz−Budapest version of the ACES II program system.[24] The diagonal Born−Oppenheimer Correction (DBOC) calculations were carried out with the Austin−Mainz−Budapest version of the ACES II program system or with the PSI3[25] open source quantum chemistry code. A few anharmonic force field calculations as well as some large-scale SCF calculations were carried out with a modified version of GAUSSIAN 03, revision C.01.[26]

Unless otherwise noted, all basis sets employed belong to the correlation consistent family of Dunning and co-workers.[27−31] For the SCF, valence CCSD, and CCSD(T) single point calculations, we combined the regular cc-pV*n*Z basis sets[27] on hydrogen with aug-cc-pV*n*Z basis sets[28] on oxygen and fluorine, and aug-cc-pV(*n*+*d*)Z basis sets[29] on chlorine. For convenience, we will denote this combination by AV*n*Z, and regular cc-pV(*n*+*d*)Z on all atoms by PV*n*Z. For the valence post-CCSD(T) calculations the PV*n*Z basis sets were employed. In the CCSD(T) core-valence correlation calculations, the augmented version of the core-valence weighted correlation consistent basis sets of Peterson and Dunning were employed,[30] while the regular (nonaugmented) version was used for the post-CCSD(T) core-valence contributions. Scalar relativistic calculations were carried out with the Pacific Northwest National Laboratory (PNNL) Douglas-Kroll-Hess relativistically contracted correlation basis sets.[31]

The ROHF-SCF contribution is extrapolated by using the Karton−Martin[32] modification of Jensen's extrapolation formula.[33] All other extrapolations are carried out by using the $A + B/L^{\alpha}$ two-point extrapolation formula (where L is the highest angular momentum present in the basis set). The ROCCSD valence contribution is partitioned into singlet-pair energies, triplet-pair energies, and $\hat{T}_1$ terms.[34] The singlet- and triplet-pair energies are extrapolated with $\alpha_S = 3$ and $\alpha_T = 5$, respectively, while the $\hat{T}_1$ term (which exhibits very weak basis set dependence), is simply set equal to that in the largest basis set. All other extrapolations are carried out with $\alpha = 3$.[20,35]

The zero-point vibrational energies (ZPVE) for OClO, ClOO, Cl_2O_2, ClO_3, $HClO_2$, and $HClO_3$ were obtained by combining CCSD(T)/PVQZ harmonic frequencies with a quartic force field calculated at the B3LYP/pc-2 level of theory, using the simplified[36] formula of Allen and co-workers. Here, pc-2 is one of the polarization consistent basis sets of Jensen.[37] Corrections for differences between isotopic average and most abundant isotopomer were also calculated using GAUSSIAN 03, Revision C.01.[26]

Unless otherwise indicated we converted the total atomization energy at absolute zero (TAE_0) to $\Delta H^{o}_{f,0}$ using the Active Thermochemical Tables (ATcT)[38−40] atomic heats of formation at 0 K ($\Delta H^{o}_{f,0}$[H(g)] = 51.633 ± 0.000, $\Delta H^{o}_{f,0}$[O(g)] = 58.997 ± 0.000, and $\Delta H^{o}_{f,0}$[F(g)] = 18.456 ± 0.036 kcal/mol, $\Delta H^{o}_{f,0}$[Cl(g)] = 28.590 ± 0.000). For the conversion of $\Delta H^{o}_{f,0}$ to 298 K (within the rigid rotor harmonic approximation) the heat content function ($H^{o}_{298} - H^{o}_{0}$) was taken from CCCBDB,[41] or otherwise (for F_2O_2, Cl_2O_2, ClO_3, $HClO_2$, and $HClO_3$) calculated at the B3LYP/pc-2 level of theory.

The W*n* family of methods W2.2, W3.2, W4lite, W4, W4.2, W4.3, and W4.4 used in the present study provides a sequence of converging computational thermochemistry protocols. A detailed description and rationalization of the W*n* protocols is given elsewhere.[20,35,42,43] In short, W4 theory represents an approximation to the relativistic basis-set limit CCSDTQ5 energy. Geometries are optimized at the CCSD(T)/PVQZ level of theory (frozen core). The SCF and valence CCSD contributions to the TAE are extrapolated from AV5Z and AV6Z basis sets, and the valence parenthetical triples (T) contribution from AVQZ and AV5Z basis sets. The higher order connected triples, $\hat{T}_3$-(T), valence correlation contribution is extrapolated from the PVDZ and PVTZ basis sets. As for the connected quadruple, $\hat{T}_4$, term, the (Q) and T_4-(Q) corrections are calculated with the PVTZ and PVDZ basis sets, respectively, both scaled by 1.1. This formula offers a very reliable as well as fairly cost-effective estimate of the basis set limit $\hat{T}_4$ contribution.[20,35] The $\hat{T}_5$ contribution is calculated using the sp part of the PVDZ basis set (denoted PVDZno*d*). The CCSD(T) inner-shell contributions are extrapolated from aug-cc-pwCV*n*Z basis sets (n = T, Q). Scalar relativistic contributions (second-order Douglas−Kroll−Hess approximation)[44] are obtained from the difference between nonrelativistic CCSD(T)/AVQZ and CCSD(T)/aug-cc-pVQZ-DK calculations. Atomic and molecular first-order spin−orbit coupling terms are taken from the experimental fine structure. Finally, the diagonal Born−Oppenheimer correction (DBOC) is calculated at the ROHF/AVTZ level of theory.

W4.2 theory[20] in addition takes account of the $\hat{T}_3$-(T) correction to the core-valence contribution computed with the cc-pwCVTZ basis set. In W4.3[20] all the valence post-CCSD(T) corrections are additionally upgraded—the $\hat{T}_3$-(T) and (Q) corrections are extrapolated from PVTZ and PVQZ basis sets, the $\hat{T}_4$-(Q) and T_5 corrections are calculated with PVTZ and PVDZ basis sets, respectively, and the $\hat{T}_6$ correction is calculated with the PVDZno*d* basis set. Finally, a correlation term at the CISD/cc-pVDZ level of theory is added to the DBOC. Turning to the lower cost methods, W4lite is the same as W4 without the valence post-CCSDT(Q) contributions. W3.2 in addition uses smaller basis sets for the SCF, valence CCSD, and CCSD(T) contributions, and W2.2 additionally omits the valence post-CCSD(T) contributions altogether.

Agreement between W4 and the latest experimental data obtained from (ATcT) is quite remarkable. For a set of 25 first- and second-row small molecules W4 obtains a mean average deviation (MAD) and root-mean-square deviation (rmsd) of 0.066 and 0.085 kcal/mol, respectively, implying a 95% confidence interval of 0.16 kcal/mol.[20] A mean signed deviation (MSD) of −0.01 kcal/mol suggests that W4 is free of systematic bias. In the same paper,[20] the following rmsds for related methods were reported: W3.2 0.16 kcal/mol, W4lite 0.12 kcal/mol, and W4.2 0.07 kcal/mol; the rmsd of W2.2 for the same data set (not reported in ref 20) is 0.85 kcal/mol, dropping to 0.36 kcal/mol upon elimination of the strongly multireference species N_2O, NO_2, and O_3. Finally, for the most rigorous member of the family, W4.4, an rmsd of just 0.05 kcal/mol has been reported,[35] compared to 0.07 kcal/mol for W4.3 over the same sample.[35]

Throughout the present paper, uncertainties on calculated values will be taken as twice said rmsds, i.e., approximate 95% confidence intervals at that level of theory.

III. Results and Discussion

In the present study the following species are considered in detail: XO, XOH, XOO, XOX, XOOX, OClO, ClO_3, and $HClO_n$ (X = H, F, Cl; n = 2−4). Our results are gathered in the following tables. Diagnostics for NDC are presented in Table 1. Tables 2 and 3 show the theoretical and experimental equilibrium geometries. Tables 4, 5, and 6 give an overview of basis set convergence of various valence and core-valence components. A component breakdown of the final W4 data is given in Table 7. The final TAEs at the various W*n* levels are

TABLE 1: Diagnostics for Importance of Nondynamical Correlation

	%TAE$_e$				CCSD(T)/cc-pVTZ		
	[SCF][a]	[(T)][a]	[post-CCSD(T)][a]	[$T_4 + T_5$][a]	T_1 diagnostic	D_1 diagnostic	largest T_2 amplitudes
HOO[b]	43.2	4.63	0.30	0.39	0.04	0.12	0.05
HOOH[b]	53.1	3.34	0.07	0.28	0.01	0.02	0.06
HOF[b]	39.2	5.15	0.22	0.48	0.01	0.04	0.09
FOF[b]	−32.2	14.59	0.95	1.58	0.01	0.04	0.07
FO[b]	−23.1	12.97	1.44	1.12	0.03	0.10	0.10
FOO[b]	−16.7	15.32	2.24	2.33	0.04	0.14	0.17
F_2O_2[b]	−32.0	16.92	1.19	1.68	0.03	0.09	0.07
ClO[b]	14.6	9.71	1.02	0.97	0.04	0.14	0.06
Cl_2O[b]	11.2	10.91	0.32	1.19	0.01	0.04	0.06
OClO[b]	−8.4	13.55	0.48	1.49	0.02	0.06	0.06
ClOO[b]	−10.3	15.35	2.74	2.66	0.04	0.14	0.19
HOCl[b]	52.2	4.08	0.08	0.36	0.01	0.02	0.06
Cl_2O_2[c]	0.1	12.20	0.34	1.20	0.02	0.06	0.04
ClO_3[c]	−15.4	14.08	0.37	1.41	0.02	0.06	0.04
$HClO_2$[c]	28.9	7.53	0.30	0.74	0.02	0.09	0.06
$HClO_3$[c,d]	25.0	8.15	0.21	0.77	0.02	0.08	0.04
$HClO_3$[e,f]	24.7	8.22	N/A	N/A	0.02	0.08	0.05
$HClO_4$[e]	67.6	2.28	N/A	N/A	0.02	0.06	0.04

[a] Percentages of the total atomization energy related to nonrelativistic, clamped-nuclei values with inner shell electrons constrained to be doubly occupied. [b] From W4 theory. [c] From W4lite theory. [d] First order saddle point for rotation of the hydroxyl group (C_s symmetry). [e] From W2.2 theory. [f] Ground state (C_1 symmetry).

compared in Table 8, and our recommended heats of formation are compared with experimental values in Table 9. Finally, the performance of various DFT exchange-correlation functionals is compared in Table 10.

A. Diagnostics for Nondynamical Correlation. The percentage of the nonrelativistic, clamped-nuclei total atomization energy at the bottom of the well (TAE$_e$) accounted for by SCF, (T) triples, post-CCSD(T), and $\hat{T}_4 + \hat{T}_5$ contributions are reported in Table 1, together with the coupled cluster T_1 and D_1 diagnostics[45,46] and the largest T_2 amplitudes. The percentage of the total atomization energy accounted for by parenthetical connected triple excitations, %TAE[(T)], has been shown to be a reliable diagnostic for the importance of NDC effects.[20]

%TAE[$\hat{T}_4 + \hat{T}_5$], the percentage of the atomization energy accounted for by connected quadruple and quintuple excitations, could be seen as an "operational definition" of the importance of NDC effects: in systems with very mild to mild NDC, CCSD(T) is generally very close to full CI quality, while in systems with strong NDC, both %TAE[$\hat{T}_4 + \hat{T}_5$] and %TAE[$\hat{T}_3$-(T)] (i.e., the percentage of TAE accounted for by higher order connected triples) are large. As the two contributions tend to partially cancel (they are of similar orders of magnitude, but connected quadruples universally increase TAE while higher order triples generally decrease it[20, 35,43,78]), looking at %TAE[FCI-CCSD(T)] may obscure the NDC phenomena.

Except for ClO and Cl_2O, all the nonhydride species considered in the present work are metastable at the SCF level. Furthermore, the percentages of the TAE$_e$ accounted for by (T) triples and $\hat{T}_4 + \hat{T}_5$ are above 10% and 1%, respectively. In particular, OClO, F_2O, F_2O_2, FO_2, and ClOO have $1.5 \leq$ %TAE[$\hat{T}_4 + \hat{T}_5$] ≤ 2.7. Such high percentages of the TAE$_e$ accounted for by (T) triples and $\hat{T}_4 + \hat{T}_5$ are typical for strongly multireference cases such as B_2, C_2, and BN. As in the original W4 paper[20] (for different systems), we find a fairly strong correlation ($R = 0.91$) between %TAE[(T)] and %[$\hat{T}_4 + \hat{T}_5$], confirming the usefulness of the %TAE[(T)] diagnostic as a gauge for the importance of higher order correlation effects. Even %TAE[SCF], the percentage of the total atomization energy accounted for at the Hartree−Fock level, is more useful as a low-cost predictor of severe NDC effects than the T_1 and D_1 diagnostics or the largest T_2 amplitudes.

F_2O_2 is a notoriously multireference system.[11,13,14] Kraka[13] employed MP*n* ($n = 2-6$) geometry optimizations at the basis set limit to study the importance of electron correlation on the equilibrium geometry of F_2O_2. They showed that inclusion of electron correlation at the MP*n* ($n = 2-4$) levels fails to qualitatively reproduce the correct ground-state geometry, implying that three-electron correlation and pair−pair correlation effects are insufficient to describe the correct electron distribution in F_2O_2. The experimental r_g geometry of Hedberg[47] is reproduced basically exactly at the MP6/CBS level of theory, indicating that coupling between three-electron and connected four-electron correlation effects plays an important role for a balanced description of anomeric delocalization and lone pair−lone pair repulsion in F_2O_2.

The hydride systems exhibit much milder NDC effects: %TAE[(T)] varies between 2.3% and 8.2%, where $HClO_4$ and $HClO_3$ correspond to the lower and upper bounds of this interval, respectively.

We note that in most cases, the T_1 and D_1 diagnostics are fairly poor predictors for the importance of post-CCSD(T) contributions to the TAEs. For instance, T_1 is 0.04 for HO_2, ClO, ClOO, and FO_2, despite the latter two having almost an order of magnitude greater %TAE[$\hat{T}_4 + \hat{T}_5$] than HO_2. The D_1 diagnostic is deceptively high (0.12) for HO_2 and deceptively low (0.04) for F_2O. The largest T_2 amplitudes are also poor predictors: e.g., they are just 0.06 for H_2O_2, HOCl, $HClO_2$, ClO, Cl_2O, and OClO, while the %TAE[$\hat{T}_4 + \hat{T}_5$] varies between 0.3% and 1.5% in the specified order.

B. Equilibrium Structures. FO_2 and F_2O_2 have unusual geometries in that the O−O bonds (∼1.2 Å) are shorter then the typical peroxide bond by about 0.2 Å, while the F−O bonds (∼1.6 Å) are longer than that in FO by about 0.2 Å. These irregularities can be attributed to anomeric delocalization of one of the lone pairs on oxygen into the antibonding σ^* orbital of the neighboring O−F bond. The anomeric effect is less pronounced in Cl_2O_2, i.e., the O−O bond (∼1.4 Å) has a typical peroxide bond length while the Cl−O bond (∼1.7 Å) is only

TABLE 2: CCSD(T)/PV(Q+d)Z and Experimental[a] Geometries (in angstroms and degrees)

			r(OX)	r(OO)	r(OH)	α[b]	τ
HOO	C_s	theor		1.330	0.970	104.23	
		exptl		1.33054(85)	0.9707(2)	104.29(31)	
HOOH	C_2	theor		1.452	0.963	99.91	112.45
		exptl		1.4556	0.967	102.32	113.70
FO	$C_{\infty v}$	theor	1.353				
		exptl	1.3541				
FOF	C_{2v}	theor	1.406			103.10	
		exptl	1.4053(4)			103.07(5)	
FOO	C_s	theor	1.632	1.192		110.91	
		exptl	1.649(13)	1.200(13)		111.19(36)	
FOOF	C_2	theor	1.532	1.234		108.46	87.52
		exptl[c]	1.586(2)	1.216(2)		109.2(2)	88.1(4)
		exptl[d]	1.575(3)	1.217(3)		109.5(5)	87.5(5)
HOF	C_s	theor	1.435		0.966	97.78	
		exptl	1.4350(31)		0.9657(16)	97.54(50)	
ClO	$C_{\infty v}$	theor	1.575				
		exptl	1.56963				
ClOCl	C_{2v}	theor	1.701			110.97	
		exptl	1.69587(7)			110.886(6)	
ClOO	C_s	theor	2.032	1.208		115.37	
		exptl	2.084(1)	1.206(2)		115.4(1)	
ClOOCl	C_2	theor	1.717	1.403		109.40	83.18
		exptl	1.7044(10)	1.4259(21)		110.07(1)	81.03(8)
HOCl	C_s	theor	1.694		0.964	102.65	
		exptl	1.6891(2)		0.9643(5)	102.96(8)	
OClO	C_{2v}	theor	1.473			117.49	
		exptl	1.469839(13)			117.4033(27)	
ClO_3[e]	C_{3v}	theor	1.445			114.21	
		exptl	1.500(1)			113.5(2.0)	
$HClO_2$[f,g]	C_1	theor	1.694		0.967	104.04	80.31
$HClO_3$[f,h,i]	C_s	theor	1.678		0.973	103.69	59.26
$HClO_3$[f,j]	C_1	theor	1.689		0.970	102.52	118.32, −0.42
$HClO_4$[f]	C_s	theor[k]	1.628		0.970	105.21	
		exptl[l]	1.641(2)		0.98	105.0	

[a] HOO from ref 121; HOOH from ref 122; FO from ref 123; FOF from ref 124; FOO from ref 48; HOF from ref 125; ClO from ref 126; Cl_2O from ref 127; ClOO from ref 128; Cl_2O_2 from ref 50 (note: "r_0" structure); HOCl from ref 129; OClO from ref 130; ClO_3 from ref 131; $HClO_4$ from ref 51 (note: "r_a" structure). Parentheses indicate uncertainty in the last digits. [b] Unless otherwise indicated α is the angle subtended at the center atom as shown in the first column. [c] "r_g" structure from ref 47. [d] "r_s" structure from ref 58. [e] $\alpha = \angle$OClO. [f] $\alpha = \angle$ClOH. [g] r(OX) = r(Cl−OH), r(HOCl−O) = 1.503, ∠OClO = 111.91. [h] r(OX) = r(Cl−OH), r(HOCl−O) = 1.439 (× 2), ∠HO−Cl−O = 104.18 (×2), τ = ∠HOClO. [i] First order saddle point for rotation of the hydroxyl group. [j] r(HOCl−O) = 1.444 and 1.4305, ∠HO−Cl−O = 101.86 and 103.17, τ = ∠HOClO (×2). [k] r(OX) = Cl−OH; r(O−ClOH) = 1.412 (×2), 1.403; ∠OClO = 115.05 (×2), 113.61; ∠HO−Cl−O = 105.06 (×2), 101.00. [l] r(OX) = Cl−OH; r(O−ClOH) = 1.404(1) (×2), 1.414(1); ∠OClO = 115.0(2) (×2), 114.60(2); ∠HO−Cl−O = 104.2(8) (×2), 101.50(0.15).

~0.1 Å longer than that in ClO. In contrast, in ClOO the O−O bond length is similar to that in FOO and F_2O_2 while the Cl−O bond is a whopping ~0.4 Å longer than that in ClO. X_2O_2 (X = H, F, Cl) are similar in that they all assume a nonplanar (C_2) geometry where the O−X bonds are approximately perpendicular to one another, in order to minimize lone pair−lone pair repulsions between the adjacent oxygens.

Table 2 lists the theoretical CCSD(T)/PVQZ (frozen core) and experimental equilibrium geometries. The geometries of XO, HOX, XOX, OClO, HO_2, and H_2O_2 (X = F, Cl) are in good agreement with the experimental geometries (bond lengths agree to 0.005 Å or better). Our theoretical bond lengths for FO_2 agree with the experimental r_e distances derived from a high-resolution IR study[48] to within the error limits of the experiment (±0.013 Å).

In the case of F_2O_2, it has been suggested (see above) that CCSD(T) or similar methods cannot accurately reproduce the F_2O_2 experimental geometry by using standard correlation consistent basis sets.[13] Compared to the gas phase electron diffraction "r_g" structure[47] our CCSD(T)/PVQZ F−O and O−O distances are 0.054 Å too short and 0.018 Å too long, respectively, in line with previous theoretical studies.[13,11] Using the AVQZ basis set slightly reduces the discrepancy but does not improve the situation fundamentally (F−O and O−O distances are 0.047 Å too short and 0.013 Å too long, respectively).[11] According to Feller and Dixon (FD),[11] neither do going up to the AV5Z basis set nor adding a core-valence correction at the CCSD(T)/cc-pCVQZ level.

This begs the question as to how would higher order connected triple excitations and noniterative connected quadruple excitations affect the geometry optimization. For want of a code that can efficiently handle such geometry optimizations, we resorted to a simple Newton−Raphson minimum search where a step of ±0.001 Å was used for the numerical differentiation and the ∠FOO and ∠FOOF angles were kept fixed at their CCSD(T) optimum values. We carried out CCSDT optimizations with the PVDZ and AVDZ basis sets in addition to a CCSDT(Q)/PVDZ optimization: the final results are summarized in Table 3 along with the corresponding SCF, CCSD, and CCSD(T) geometries. In general it can be seen that with the PVDZ basis set the F−O bond length increases and the O−O bond length decreases with the level of electron correlation used. The F−O bond length is much more sensitive to post-CCSD(T) correlation effects then the O−O bond length (for example, the former increases by 0.06 Å and the latter decreases by 0.005 Å when passing from CCSD(T)/PVDZ to

TABLE 3: CCSDT and CCSDT(Q) Equilibrium Geometries of FOOF (in angstroms and degrees)

	r(OF)	*r*(OO)	α(FOO)	τ(FOOF)
SCF/PVDZ	1.368	1.304	106.0	84.4
CCSD/PVDZ	1.489	1.286	107.0	86.4
CCSD(T)/PVDZ	1.642	1.215	109.5	88.2
CCSDT/PVDZ	1.641	1.217	109.5[a]	88.2[a]
CCSDT(Q)/PVDZ	1.702	1.210	109.5[a]	88.2[a]
SCF/AVDZ	1.362	1.299	105.9	85.2
CCSD/AVDZ	1.490	1.275	106.9	87.0
CCSD(T)/AVDZ	1.628	1.210	109.2	88.7
CCSDT/AVDZ	1.62_0[b]	1.21_4[b]	109.2[c]	88.7[c]
CCSD(T)/AV5Z[d]	1.539	1.228	108.6	88.1
Δpost-CCSD(T)[e]	0.061	−0.005	N/A	N/A
ΔCV[f]	−0.002	−0.001	0.0	0.4
best est. r_e[g]	1.597	1.221	108.6	87.7
$r_z - r_e$[h]	0.003	0.007	0.03	0.06
exptl r_g[i]	1.586	1.216	109.2	88.1

[a] Fixed at the CCSD(T)/PVDZ value during the geometry optimization. [b] Converged only to 0.01 Å due to numerical instabilities. [c] Fixed at the CCSD(T)/AVDZ value during the geometry optimization. [d] From ref 11 (note: angles at the CCSD(T)/AVQZ level of theory). [e] Taken as the CCSDT(Q)/PVDZ−CCSD(T)/PVDZ difference in bond lengths. [f] Taken as the CCSD(T)(ae)/aug-cc-pwCVTZ−CCSD(T)(fc)/aug-cc-pVTZ difference in bond lengths. [g] CCSD(T)/AV5Z + Δpost-CCSD(T) + ΔCV. [h] From a B3LYP/aug-pc2 anharmonic force field calculation. [i] Gas-phase electron-diffraction "r_g" structure from ref 47.

CCSDT(Q)/PVDZ, where practically all of the change comes from the noniterative connected quadruple excitations). It can also be seen that addition of diffuse functions to the PVDZ basis set decreases both bond lengths, something a bit more pronounced for the F−O bond at the CCSD(T) and CCSDT levels.

Taking the CCSD(T)/AV5Z geometry of FD[11] and adding to it a post-CCSD(T) correction term taken as the CCSDT(Q)/PVDZ−CCSD(T)/PVDZ difference in bond lengths, as well as a core-valence correction term taken as the CCSD(T)/aug-cc-pwCVTZ−CCSD(T)/aug-cc-pVTZ difference in bond lengths, we obtain F−O and O−O bonds that are 0.011 and 0.005 Å longer then the experimental r_g bond lengths (see Table 3). The post-CCSD(T) correction of 0.06 Å for the F−O bond is perhaps the weakest premise in the above argument and should be regarded as an upper limit (for the PVDZ basis set) because of use of CCSDT(Q) rather than the fully iterative $\hat{T}_4$. Furthermore, for a more precise comparison with the r_g bond lengths, vibrational averaging effects must also be taken into account: typically this will increase r_e due to cubic anharmonicity of the potential energy surface. For the purpose of illustration, the calculated $r_z - r_e$ differences from a B3LYP/aug-pc2 anharmonic force field calculation are 0.003 and 0.007 Å for the F−O and O−O bonds, respectively.

As for Cl_2O_2, our CCSD(T)/PVQZ ground-state geometry is very close to the CCSD(T)/AVQZ geometry reported by Peterson,[49] supporting their conjecture that diffuse functions have only a minor effect on the CCSD(T) equilibrium geometry optimization. An experimental r_0 microwave structure has been reported.[50] Our theoretical Cl−O bond length is 0.01Å longer, and the O−O bond length 0.02 Å shorter, than the experimental r_0 values. In this case, B3LYP/aug-pc2 anharmonic $r_z - r_e$ differences amount to 0.005 Å for both bonds.

From the molecules considered in the present study, the largest discrepancies between theory and experiment are found for ClOO and ClO_3. The theoretical Cl−O bond distances are 0.05 and 0.055 Å shorter than experiment for ClOO and ClO_3, respectively.

Our theoretical bond distances for $HClO_4$ agree with the experimental r_a distances, derived from a gas-phase electron diffraction study,[51] to within 0.01 Å. Unsurprisingly, this molecule has no strong static correlation effects.

C. SCF Component of the TAE. The SCF component of the TAE for all first-row systems is, as expected, practically converged with the AV{Q,5}Z basis set pair (Table 4). For the chlorine systems, however, convergence becomes markedly slower as the formal oxidation state of the chlorine atom is higher. In particular, there is a very strong dependence on the presence of high-exponent *d* and *f* functions in the basis set due to inner polarization effects.[29,52,53] The relation between the effect extra *d* and *f* functions have on the SCF component and the formal oxidation state of the chlorine atom is illustrated in Table 5. An almost linear correlation exists between the formal oxidation state of the chlorine atom and the extent to which the addition of tight *d* and *f* functions affects the SCF component of the binding energy. This can be regarded as a quantitative measure of the importance of back-donation from the oxygen lone pair orbitals into the 3*d* Rydberg orbital of the chlorine atom.[53]

Practically speaking, for the purposes of the present study, we observe that the AV{5,6}+dZ limits (as used in W4lite and higher theories) underestimate the aug′-cc-pV{5,6}Z+2d1f results by very small amounts: 0.01 kcal/mol for $HClO_2$ and OClO, by 0.02 kcal/mol for $HClO_3$ and ClO_3, by 0.03 kcal/mol for $HClO_4$, and by 0.00 kcal/mol for all of the other chlorine systems considered in the present work. It should be noted that the AV{Q,5}+dZ extrapolated results (as used in W2.2 and W3.2 theories) underestimate the aug′-cc-pV{5,6}Z+2d1f limits by 0.02, 0.04, 0.05, 0.06, 0.07, 0.15, 0.25, 0.39, 0.47, and 0.66 kcal/mol, respectively, for ClOO, HOCl, ClO, Cl_2O_2, Cl_2O, $HClO_2$, OClO, $HClO_3$, ClO_3, and $HClO_4$. Thus, for molecules for which we were only able to apply W2.2 theory (namely, $HClO_3$ and $HClO_4$), the SCF component has been extrapolated from the aug′-cc-pV{5,6}Z+2d1f basis set pair.

D. Overview of Valence Contributions. Table 4 gives an overview of basis set convergence of various valence components. For the fluorine systems, the CCSD contribution extrapolated from the AV{Q,5}Z pair systematically underestimates the AV{5,6}Z results (by ∼0.10 kcal/mol for HOF and FO, ∼0.2 kcal/mol for F_2O and FO_2, and 0.30 kcal/mol for F_2O_2) where, as expected, the lion's share of these differences comes from the singlet-pairs contributions. For the chlorine systems convergence of the CCSD component is faster and, with the exception of ClOO, the AV{Q,5}Z pair systematically overestimates the AV{5,6}Z results by 0.1 kcal/mol.

In a recent publication,[35] it was shown that the (T) triples correction to the TAE extrapolated from the AV{T,Q}Z basis set pair is in very good agreement with basis set limit results. Our results for all the systems considered here are consistent with this observation: in general, the extrapolated AV{T,Q}Z data systematically underestimate the AV{Q,5}Z (or where available AV{5,6}Z) results by 0.00−0.04 kcal/mol and the largest discrepancies are 0.06 kcal/mol for ClOO and Cl_2O_2.

Higher order triples contributions, as observed previously,[20,43,78] generally decrease the binding energies and vary (in absolute value) between 0.1 kcal/mol in FO_2 to 1.8 kcal/mol in ClO_3 (Table 4). Nevertheless, for a few systems (all of them radicals) they increase the binding energies: specifically, we find (in kcal/mol) 0.03 for ClO, 0.10 for ClOO, and 0.17 for FO. For the smaller systems (OX and HOX; X = F, Cl) we were able to obtain the higher order connected triples, $\hat{T}_3$-(T), correction with the PVQZ basis set. The PV{D,T}Z numbers

TABLE 4: Overview of Convergence of Different Valence Contributions (TAE, in kcal/mol)[e]

	SCF			CCSD		(T)			$\hat{T}_3$-(T)		(Q)			$\hat{T}_4$-(Q)		$\hat{T}_5$		$\hat{T}_6$
	(b)	(c)	(d)	(b)	(c)	(a)	(b)	(c)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(g)	(l)
HO_2	75.69	75.70		90.88	90.94	8.11	8.11		−0.17		0.71	0.70	0.77	−0.12		0.04	0.05	
H_2O_2	142.62	142.62		116.86	116.90	9.00	8.98		−0.55		0.81	0.75		−0.11		0.03		
HOF	62.12	62.13		87.72	87.80	8.16	8.16		−0.41	−0.40	0.79	0.74	0.80	−0.10		0.04	0.04	0.005
F_2O	−30.21	−30.21		109.30	109.52	13.68	13.71		−0.59		1.48	1.47		−0.23		0.10		
FO	−12.23	−12.23		57.49	57.59	6.86	6.87	6.86	0.17	0.28	0.65	0.64	0.70	−0.16	−0.20	0.04	0.03	0.001
FO_2	−22.49	−22.48		133.34	133.54	2.61	2.64		−0.12		3.00	3.24		−0.66		0.23[c]		
F_2O_2	−48.81	−48.79		173.43	173.73	25.79	25.82		−0.74		3.45	2.75		−0.74		0.27[c]		
ClO	9.44	9.48	9.48	48.75	48.69	6.29	6.33	6.31	0.03	0.03	0.46	0.63	0.71	−0.07	−0.12	0.02	0.04	0.003
Cl_2O	11.30	11.36	11.36	78.64	78.55	11.02	11.05		−0.88		0.97	1.21		−0.17		0.04		
OClO	−11.01	−10.77	−10.76	120.61	120.52	17.28	17.30		−1.28		1.88	1.96		−0.38		0.12		
ClOO	−13.02	−13.00	−13.00	116.49	116.56	19.35	19.41		0.10		2.88	3.40		−0.61		0.22		
Cl_2O_2	0.14	0.19	0.20	130.16	130.15	18.13	18.19		−1.29		1.80							
HOCl	86.67	86.70	86.70	72.42	72.35	6.76	6.77	6.75	−0.47	−0.49	0.54	0.59		−0.07	−0.07[b]	0.02		0.004[d]
ClO_3	−26.46	−26.01	−25.99	170.94	170.84	23.80	23.84		−1.76		2.39							
$HClO_2$	58.92	59.07	59.07	128.95	128.86	15.37	15.38		−0.91		1.52							
$HClO_3$[a]	67.78	68.15	68.17	181.69	181.57	22.18	22.20		−1.54		2.11							
$HClO_3$	67.21	67.58	67.60	182.45		22.35												
$HClO_4$	79.89	80.52	80.55	227.42		26.46												

[a] First order saddle point for rotation of the hydroxyl group (C_s symmetry). [b] The CCSDTQ/PVTZ calculation converged only to 0.016 kcal/mol. [c] Here $\hat{T}_5 \approx$ CCSDTQ(5)$_\Lambda$−CCSDTQ. [d] Here $\hat{T}_6 \approx$ CCSDTQ5(6)$_\Lambda$−CCSDTQ5. [e] (a) AV{T,Q}Z; (b) AV{Q,5}Z; (c) AV{5,6}Z; (d) aug-cc-pV{5,6}Z+2d1f; (e) PV{D,T}Z; (f) PV{T,Q}Z; (g) PVDZ; (h) PVTZ; (i) PVQZ; (j) 1.10 × [RCCSDTQ/PVDZ−UCCSDT(Q)/PVDZ]; (k) UCCSDTQ/PVTZ−UCCSDT(Q)/PVTZ; (l) PVDZ *nod*.

TABLE 5: Basis Set Convergence of the SCF Contribution to the Total Atomization Energies (in kcal/mol) of a Few Chlorine Compounds with Formal Oxidation State of the Chlorine Ranging from +1 to +7

		AVDZ	AVTZ	AVQZ	AV5Z	AV6Z	AV{Q,5}Z[a]	AV{5,6}Z[a]	AV{Q,5}Z[b]	AV{5,6}Z[b]
					HF/aug′-cc-pV(n+*d*)Z−HF/aug′-cc-pVnZ differences					
1	HOCl	1.79	0.94	0.57	0.11	0.04	0.03	0.03	−0.11	0.00
2	$HClO_2$	8.36	4.50	2.66	0.54	0.21	0.18	0.14	−0.49	−0.02
4	OClO	14.94	7.97	4.63	0.96	0.36	0.35	0.24	−0.83	−0.04
5	$HClO_3$	22.52	12.01	6.95	1.44	0.54	0.51	0.36	−1.25	−0.06
6	ClO_3	28.59	15.23	8.77	1.84	0.69	0.67	0.45	−1.54	−0.08
7	$HClO_4$	40.22	21.10	12.06	2.51	0.94	0.91	0.62	−2.14	−0.11
					HF/aug′-cc-pVnZ+2*d*1*f*−HF/aug′-cc-pV(n+*d*)Z differences					
1	HOCl	0.48	0.07	0.08	0.05	0.01	0.04	0.00	0.03	−0.02
2	$HClO_2$	2.48	0.45	0.34	0.19	0.04	0.16	0.01	0.11	−0.06
4	OClO	4.91	0.87	0.58	0.31	0.06	0.26	0.01	0.18	−0.11
5	$HClO_3$	7.02	1.42	0.86	0.48	0.09	0.41	0.02	0.29	−0.16
6	ClO_3	8.84	1.72	1.07	0.58	0.12	0.50	0.02	0.35	−0.20
7	$HClO_4$	11.79	2.51	1.42	0.80	0.16	0.70	0.03	0.50	−0.27
					HF/aug′-cc-pVnZ+4*d*1*f*−HF/aug′-cc-pVnZ+2*d*1*f* differences					
1	HOCl	0.15	0.03	0.02						
2	$HClO_2$	0.71	0.18	0.08						
4	OClO	1.29	0.32	0.13						
5	$HClO_3$	1.92	0.49	0.20						
6	ClO_3	2.43	0.62	0.25						
7	$HClO_4$	3.35	0.88	0.35						

[a] Extrapolated with the Karton−Martin extrapolation formula. [b] Extrapolated with the $A + B/L^5$ extrapolation formula.

are very close to the PV{T,Q}Z results for ClO, HOF, and HOCl, but for FO they underestimate by about 0.1 kcal/mol.

Turning to the parenthetical connected quadruple excitations, the (Q) contribution to the TAE can get quite hefty, ranging from 0.6 kcal/mol in HOCl to 3.4 kcal/mol in ClOO. With the main exception of F_2O_2, the contribution increases monotonically with basis set size from PVDZ onward. For systems for which we have PVQZ results (namely FO, HOF, OCl, and HO_2) the PV{D,T}Z basis set pair underestimates the PV{T,Q}Z results by ~0.10 kcal/mol. For the chlorine systems for which we have PVTZ results the PVDZ basis set (used in W3.2 and W4lite theories) substantially undershoots the basis set limit results (estimated by 1.1 × PVTZ, as used in W4 and W4.2 theories)[20] by 0.11, 0.23, 0.27, 0.36, and 0.86 kcal/mol for HOCl, ClO, OClO, Cl_2O, and ClOO, respectively. This is consistent with earlier observations regarding second-row molecules in general.[43,35] As for the first row systems, the PVDZ basis set performs rather well except for FO_2 and F_2O_2—where it underestimates the 1.1 × PVTZ results by 0.56 kcal/mol for the former and overestimates by 0.43 kcal/mol for the latter. On the accuracy scale that post-CCSD(T) thermochemistry protocols like W4[20] and HEAT[78] strive for, these are unacceptable errors.

Higher order connected quadruples contributions, $\hat{T}_4$-(Q), converge rapidly with the basis set.[35] This contribution (calculated with the PVDZ basis set) systematically reduces the binding energies and varies (in absolute value) between 0.1 kcal/mol in HO_2, H_2O_2, HOF, ClO, and HOCl to 0.7 kcal/mol in FO_2 and F_2O_2 (Table 4). We note that the CCSDTQ/PVDZ

TABLE 6: Overview of Convergence of Different Core−Valence Contributions (TAE, in kcal/mol)

	CCSD			(T)			$\hat{T}_3$-(T)[a]
	ACVTZ	ACVQZ	ACV {T,Q}Z	ACVTZ	ACVQZ	ACV {T,Q}Z	CVTZ
HO_2	0.07	0.04	0.02	0.19	0.21	0.23	0.021
H_2O_2	0.15	0.13	0.11	0.21	0.23	0.25	0.025
HOF	−0.07	−0.10	−0.13	0.21	0.23	0.24	0.028
F_2O	−0.44	−0.53	−0.60	0.36	0.39	0.42	0.049
FO	−0.19	−0.23	−0.26	0.18	0.20	0.21	0.019
FO_2	−0.36	−0.45	−0.52	0.42	0.46	0.49	
F_2O_2	−0.65	−0.80	−0.91	0.57	0.63	0.67	
ClO	−0.07	−0.14	−0.19	0.32	0.35	0.37	0.012
Cl_2O	−0.18	−0.33	−0.44	0.52	0.56	0.60	
OClO	0.10	−0.04	−0.13	0.47	0.52	0.56	
ClOO	−0.51	−0.64	−0.73	0.58	0.62	0.66	
Cl_2O_2	−0.35	−0.56	−0.71	0.70	0.76	0.80	
HOCl	0.05	−0.01	−0.05	0.27	0.30	0.32	0.017
ClO_3	0.13	−0.07	−0.22	0.62	0.70	0.75	
$HClO_2$	0.05	−0.10	−0.20	0.49	0.54	0.57	
$HClO_3$	0.22	0.01	−0.14	0.63	0.70	0.76	
$HClO_4$	0.46	0.21	0.03	0.74	0.83	0.89	

[a] core[ROCCSDT,MRCC] − core[ROCCSD(T),molpro].

calculation for FOOF was especially demanding computationally, requiring 3.1 billion amplitudes and taking approximately 2 days per iteration on 8 Intel Cloverton 2.66 GHz cores with 32 GB of RAM available. About 1.5 TB of scratch disk space was in use.

Connected quintuples contributions, $\hat{T}_5$, are sufficiently converged with the PVDZno*d* basis set. This contribution is still quite significant, ranging from 0.03 to 0.27 kcal/mol, where the largest contributions (0.09, 0.13, and 0.22 kcal/mol) are found for F_2O, OClO, and ClOO, respectively. For F_2O_2 and FO_2 we were only able to obtain the $(5)_\Lambda$/PVDZno*d* contribution, which amounts to 0.27 and 0.23 kcal/mol, respectively. For OX and HOX (X = F, Cl) the connected sextuples, $\hat{T}_6$, term ranges from 0.001 to 0.005 kcal/mol.

E. Overview of Core-Valence Contributions. Table 6 gives an overview of basis set convergence of various core-valence contributions. For the halide systems, the core-valence contribution to the CCSD correlation energy is repulsive, i.e., it reduces the binding energies by amounts ranging from 0.05 kcal/mol in HOCl to 0.91 kcal/mol in F_2O_2. The CCSD(T) inner-shell contribution reduces the binding energies by 0.03, 0.05, 0.08, 0.18, and 0.24 kcal/mol in FO_2, FO, ClO_2, F_2O, and F_2O_2, respectively, and increases the binding energies by 0.1−0.9 kcal/mol for all the other systems considered (Table 7). In a previous paper[35] that included a thorough examination of post-CCSD contributions to core-valence TAEs, it was shown that: (a) parenthetical triples contributions extrapolated from ACVTZ and ACVQZ basis sets are essentially at the complete basis set limit and (b) post-CCSD(T) core-valence contributions almost universally increase the TAEs and range from basically nil for systems dominated by dynamical correlation to 0.3 kcal/mol for pathologically multireference systems such as C_2. Thus, neglecting post-CCSD(T) inner-shell effects in W4 theory might result in a slight overestimation of the TAEs for FO_2, FO, ClO_2, F_2O, and F_2O_2 and a slight underestimation for the other systems considered. For some of the smaller systems we were able to obtain post-CCSD(T) core-valence contributions: the higher order triples, $\hat{T}_3$-(T), core-valence contributions range from 0.01 kcal/mol in ClO to 0.05 kcal/mol in F_2O, while the parenthetical quadruples core-valence contributions, (Q)-$\hat{T}_3$, amount to 0.014, 0.016, and 0.036 kcal/mol in HO_2, ClO, and FO, respectively.

F. Fluorine Oxides. ***1. FO ($^2\Pi_{3/2}$).*** The W2.2 TAE_0 of oxygen monofluoride (50.2 kcal/mol) is bracketed between the KN[12] and FD[11] values of 50.3 and 50.1 kcal/mol. The valence $\hat{T}_3$-(T) contribution to the TAE, which in most cases is repulsive, is +0.17 kcal/mol at the W4 level (PV{D,T}Z) and +0.28 kcal/mol at the W4.3 level (PV{T,Q}Z). The $\hat{T}_4$ contribution is 0.65 kcal/mol at the W3.2 level and 0.55 kcal/mol at the W4 level. The W4 TAE_0 (51.07 kcal/mol) is in close agreement with the ATcT value of 51.02 ± 0.11 kcal/mol.[80] At the W4.3 and W4.4 levels we obtain 51.18 and 51.17 kcal/mol where practically all of the difference from W4 comes from the improved extrapolation of the $\hat{T}_3$-(T) contribution.

2. F_2O ($^1A_1$). The W2.2 TAE_0 of monooxygen difluoride (88.3 kcal/mol) is lower by about 0.5 kcal/mol than the KN[12] and FD[11] values. The W3.2 TAE_0 (89.15 kcal/mol) is 0.9 kcal/mol higher than the W2.2 value. The higher order triples, $\hat{T}_3$-(T), contribution amounts to −0.59 kcal/mol and the $\hat{T}_4$ contribution ((Q)/PVDZ) to 1.48 kcal/mol. Using more elaborate basis sets for the extrapolations of the SCF, CCSD, and (T) contributions in W4lite raises the TAE_0 by one-quarter of a kcal/mol (0.22 and 0.03 kcal/mol from the valence CCSD and (T) contributions) to 89.40 kcal/mol. The more rigorous $\hat{T}_4$ estimation in W4 which explicitly includes higher order quadruple contribution is 1.38 kcal/mol, while the $\hat{T}_5$ contribution amounts to 0.10 kcal/mol, in effect leaving the W4 TAE_0 identical to the W4lite value. At the W4.2 level we obtain TAE_0 = 89.43 kcal/mol, in good agreement with the Gurvich[54] TAE_0 of 89.5 ± 0.4. The W4.4 TAE_0 can be estimated by assuming that the $F_2O + H_2O \rightarrow 2HOF$ isodesmic reaction energy stays constant at the W4.2 and W4.4 levels. Following this assumption, we obtain a TAE_0 of 89.67 kcal/mol: we note that the W4.4 TAE_0 for HOF was likewise estimated via an isodesmic reaction (vide infra).

3. FO_2 ($^2A''$). At the W2.2 level, our TAE_0 (126.9 kcal/mol) is 0.5 kcal/mol higher than the value obtained by FD,[11] where again most of the difference comes from the different basis sets and extrapolations used for the CCSD(T) contribution. FO_2 is similar to systems like O_3 in that basis set limit CCSD(T) methods fail badly in reproducing the correct TAE. The W2.2 TAE_0 is 2.9 kcal/mol lower than at the W3.2 level (129.76 kcal/mol). The $\hat{T}_3$-(T) contribution comes to merely −0.12 kcal/mol, while the $\hat{T}_4$ contribution is 3.00 and 2.91 kcal/mol at the W3.2 and W4 levels, respectively. The $\hat{T}_5$ contribution further increases the TAE by 0.23 kcal/mol. Overall, post-CCSD(T) contributions add up to 3.1 kcal/mol. All in all, the W4 TAE_0 (130.15) is well within the error bar of the JANAF[55] value (129.9 ± 0.5). Assuming that the energy of the reaction $FO_2 + H_2O \rightarrow HO_2 + HOF$ stays the same at the W4 and W4.4 levels, the W4.4 TAE_0 is estimated to be 130.31 kcal/mol (note that the W4.4 TAE_0 for HO_2 was estimated via the $2HO_2 \rightarrow 2OH + O_2$ isogyric reaction).

4. F_2O_2 (^1A). Dioxygen difluoride is yet another example where the CCSD(T) limit is far from the FCI limit. The W2.2 TAE_0 of F_2O_2 (143.8 kcal/mol) is 0.6 kcal/mol higher than the value of FD,[11] 0.5 kcal/mol of which comes from the valence CCSD(T) contribution and 0.1 kcal/mol from the core-valence CCSD(T) contribution. The W3.2 TAE_0 (146.54 kcal/mol) is 2.7 kcal/mol higher than the W2.2 value. The $\hat{T}_3$-(T) contribution amounts to −0.74 kcal/mol while the (Q)/PVDZ contribution reaches 3.45 kcal/mol. The W4lite TAE_0 is 0.35 kcal/mol higher than the W3.2 value (0.02, 0.30, and 0.03 kcal/mol from the valence SCF, CCSD, and (T) contributions). The W4 overall connected quadruples contribution is 2.29 kcal/mol, over 1 kcal/mol below the (Q)/PVDZ estimate. Pronounced "overshoots"

TABLE 7: Component Breakdown of the Final W4 Total Atomization Energies at the Bottom of the Well (in kcal/mol)

	SCF	valence CCSD	valence (T)	$\hat{T}_3$-(T)	$\hat{T}_4$ (a)	$\hat{T}_5$	inner shell	relative	spin−orbit	DBOC	(b)	(c)	ΔDBOC	TAE_e[a]
HO_2	75.70	90.94	8.11	−0.17	0.65	0.04	0.24	−0.27	−0.45	0.01	0.04	0.004	−0.02	174.82
H_2O_2	142.62	116.90	8.98	−0.55	0.72	0.03	0.36	−0.37	−0.45	0.11[b]	0.05	0	−0.03	268.38
HOF	62.13	87.80	8.16	−0.41	0.72	0.04	0.11	−0.21	−0.61	0.07	0.03	0	−0.02	157.80
F_2O	−30.21	109.52	13.71	−0.59	1.38	0.10	−0.18	−0.11	−0.99	0.01[b]	0.04	0	0.00	92.66
FO	−12.23	57.59	6.87	0.17	0.55	0.04	−0.05	−0.08	−0.33	0.00	0.02	0.01	0.00	52.56
FO_2	−22.48	133.54	20.64	−0.12	2.91	0.23[c]	−0.03	−0.17	−0.83	−0.02	0.05	0.02	0.00	133.71
F_2O_2	−48.79	173.73	25.82	−0.74	2.29	0.27[c]	−0.24	−0.16	−1.22	0.01	0.06	0	N/A	151.00
ClO	9.48	48.69	6.33	0.03	0.61	0.02	0.18	−0.24	−0.61	0.00	0.03	0.002	N/A	64.51
Cl_2O	11.36	78.55	11.05	−0.88	1.16	0.04	0.15	−0.26	−1.91	0.01	0.04	0	N/A	99.31
OClO	−10.77	120.52	17.30	−1.28	1.78	0.12	0.43	−0.76	−1.29	−0.08	0.05	0.06	N/A	125.99
ClOO	−13.00	116.56	19.41	0.11	3.14	0.22	−0.08	−0.13	−1.29	0.00	0.05	0.01	N/A	124.97
HOCl	86.70	72.35	6.77	−0.47	0.58	0.02	0.26	−0.33	−1.06	0.07	0.03	0	−0.02	164.90
Cl_2O_2[d]	0.19	130.15	18.19	−1.29	1.80		0.09	−0.27	−2.13	0.01	0.07	0	N/A	146.77
ClO_3[d]	−26.01	170.84	23.84	−1.76	2.39		0.53	−1.64	−1.51	0.02	0.08	N/A	N/A	166.75
$HClO_2$[d]	59.07	128.87	15.38	−0.91	1.52		0.37	−0.61	−1.29	0.07	0.06	0	N/A	202.49
$HClO_3$[d, e]	68.15	181.57	22.20	−1.54	2.11		0.61	−1.27	−1.51	0.09	0.08	0	N/A	270.46
$HClO_3$[f, e]	68.17[g]	181.69	22.18				0.61	−1.27	−1.51	0.09		0	N/A	269.96
$HClO_3$[f]	67.60[g]	182.45	22.35				0.61	−1.26	−1.51	0.09		0	N/A	270.33
$HClO_4$[f]	80.55[g]	227.42	26.46				0.92	−2.72	−1.73	0.11		0	N/A	331.00

[a] Note that the TAE_e values do not include ΔDBOC. [b] Calculated with PSI3 rather than ACESII. [c] $\hat{T}_5 \approx$ CCSDTQ(5)$_\Lambda$/PVDZ-no*d*−CCSDTQ/PVDZno*d*. [d] From W4lite theory. [e] First order saddle point for the rotation of the hydroxyl group (C_s symmetry). [f] From W2.2 theory. [g] aug-cc-pV{5,6}Z+2d1f.

TABLE 8: Comparison between W4 Total Atomization Energies at 0 K, Active Thermochemical Tables Benchmarks, and Earlier Reference Data (kcal/mol)

	ZPVE[a]	W2.2	W3.2	W4lite	W4	W4.2	W4.3	W4.4	ATcT[b]	uncert.	CCCBDB[c]	uncert.
HO_2	8.85	165.36	165.93	166.00	165.97	165.97			165.98	0.05	166.6	0.7
H_2O_2	16.31	251.82	252.10	252.13	252.07	252.08	252.13[d]	252.05[d]	252.21	0.02	252.3	0.1
HOF	8.58	148.78	149.17	149.25	149.23	149.24	149.37[e]	149.33[e]	148.96	0.15	151.6	1.2
FO	1.50	50.17	51.00	51.12	51.06	51.07	51.18	51.17	51.02	0.11	51.6	2.4
F_2O	3.26	88.25	89.15	89.40	89.40	89.43	89.69	89.67			89.5	0.4
FO_2	3.56	126.86	129.76	130.01	130.15						129.9	0.5
F_2O_2	5.0	143.80	146.54	146.89	146.00[g]							
ClO	1.22	62.60	63.10	63.12	63.30	63.29	63.38	63.40			63.4	0.5
Cl_2O	2.37	96.59	96.70	96.71	96.93	96.94[h]	97.14[h]	97.18[h]				
OClO	3.67	121.52	122.14	122.31	122.33	122.34[i]	122.48[i]	122.47[i]			122.9	1.9
ClOO	3.08	118.25	121.26	121.41	121.88						122.7	1.0
Cl_2O_2	4.12	142.01	142.55	142.65	142.92[j]							
ClO_3	6.67	159.01	159.68	160.08	159.93[k]							
HOCl	8.18	156.60	156.69	156.67	156.72	156.73	156.83[l]	156.81[l]	156.64	0.43	156.3	0.5
$HClO_2$	10.37	191.40	192.05	192.11	192.01[m]							
$HClO_3$	12.78	257.16[n]	258.15[o]	258.05[o]								
$HClO_4$	17.64	313.35[n]										
OH	5.29	101.78	101.88	101.84	101.82	101.81	101.80	101.76	101.73	0.01	101.8	0.1
H_2O	13.26	219.44	219.52	219.46	219.39	219.38	219.38	219.32	219.37	0.01	219.4	0.1
O_2	2.25	117.22	117.61	117.77	117.88	117.89	118.01	117.96	117.99	0.00	118.0	0.0

[a] Zero-point vibrational energies: HO_2 from ref 81; H_2O_2 from ref 132, adjusted by one-half the sum of the discrepancies between observed and computed fundamentals listed there (averaged over both rotationally doubled levels); HOF experimental harmonic frequencies from ref 125 combined with theoretical anharmonicity constants from ref 82; F_2O CCSD(T)/cc-pVQZ harmonic frequencies combined with CCSD(T)/cc-pVTZ anharmonicity constants both from ref 133; FO from ref 123; FO_2 and F_2O_2 from ref 11; ClO from ref 126; Cl_2O, OClO, ClOO, Cl_2O_2, ClO_3, and $HClO_2$ see computational details; $HClO_3$ from a B3LYP/aug-pc2+2d quartic force field calculation; HOCl, OH, H_2O, and O_2 from ref 20; $HClO_4$ from ref 53. [b] References 38−40; the adjunct uncertainties correspond to 95% confidence intervals, as customary in experimental thermochemistry, which were obtained by utilizing the full covariance matrix computed by ATcT. The actual values reported here were taken from ref 80 for HO_2, H_2O_2, FO, OH, H_2O, and O_2 from ref 20 for HOCl, and from ref 77 for HOF. [c] Experimental data section of ref 41. [d] Assuming that the $2H_2O_2 \rightarrow O_2 + 2H_2$ O reaction energy is the same at the W4.2 and post-W4.2 levels. [e] Assuming that the HOF + OH → OF + H_2O isodesmic reaction energy is the same at the W4.2 and post-W4.2 levels. [f] Assuming that the $F_2O + H_2O \rightarrow 2HOF$ isodesmic reaction energy is the same at the W4.2 and post-W4.2 levels. [g] Correcting for the experimental geometry gives 145.63 kcal/mol. [h] Assuming that the $Cl_2O + H_2O \rightarrow 2HOCl$ isodesmic reaction energy is the same at the W4 and post-W4 levels. [i] Assuming that the OClO + H_2O → HO_2 + HOCl reaction energy is the same at the W4 and post-W4 levels. [j] W4 TAE_0 of Cl_2O_2 estimated from two isodesmic reactions (see text). [k] Assuming that the ClO_3 + ClO → 2OClO isodesmic reaction energy is the same at the W4lite and W4 levels. [l] Assuming that the HOCl + OH → OCl + H_2O isodesmic reaction energy is the same at the W4.2 and post-W4.2 levels. [m] Assuming that the $HClO_2$ +ClO → HOCl+OClO isodesmic reaction energy is the same at the W4lite and W4 levels. [n] Improved SCF component from the aug-cc-pV{5,6}+2d1f basis set pair. [o] Assuming that the barrier for rotation of the hydroxyl group remains unchanged at the W2.2 and postW2.2 levels (see text).

of quadruples contributions at the (Q)/PVDZ level (as used in W4lite and HEAT345-(Q)) for oxygen and fluorine compounds were noted previously:[20,35] FOOF is thus far the most extreme example we encountered.

TABLE 9: Derived Heats of Formation at 0 and 298 K Compared to Literature and Earlier Computationally Derived Values

	0 K			298 K		
	our best[a]	JANAF[b]	other exptl[c]	our best[a]	JANAF[b]	other exptl[d]
HO_2	3.65 ± 0.14	3.01 ± 0.72	3.64 ± 0.06	2.96 ± 0.14	2.32 ± 0.72	2.94 ± 0.06
H_2O_2	−30.82 ± 0.14	−31.04 ± 0.05	−31.01 ± 0.04	−32.24 ± 0.14	−32.48 ± 0.05	−32.45 ± 0.04
HOF	−20.15 ± 0.14	−22.47 ± 1.2	−20.02 ± 0.25	−20.84 ± 0.14	−23.16 ± 1.2	
FO	26.28 ± 0.11	25.9 ± 2.4		26.43 ± 0.11	26.05 ± 2.4	
F_2O	6.48 ± 0.14	6.39 ± 0.4		5.94 ± 0.14	5.86 ± 0.4	
FO_2	6.30 ± 0.16	6.50 ± 0.48		5.87 ± 0.16	6.07 ± 0.48	
F_2O_2	8.90 ± 0.18[e]	5.5 ± 0.5		7.84 ± 0.18[e]	4.6 ± 0.5	
ClO	24.19 ± 0.10	24.21 ± 0.50	24.15 ± 0.03	24.18 ± 0.10	24.19 ± 0.50	24.29 ± 0.02
HOCl	−17.51 ± 0.14	−17.09 ± 0.50	−17.68 ± 0.03 −17.4 ± 1.2	−18.20 ± 0.14	−17.81 ± 0.50	−18.36 ± 0.03
Cl_2O	19.24 ± 0.16	19.79 ± 0.48		18.82 ± 0.16	19.36 ± 0.48	18.9 ± 2.4
OClO	24.26 ± 0.16	23.66 ± 1.9		23.67 ± 0.16	23.18 ± 1.9	25.1 ± 1.4
ClOO	24.69 ± 0.32	23.83 ± 0.96		24.30 ± 0.32	23.42 ± 0.96	21.51 ± 1.2
Cl_2O_2	32.28 ± 0.3	N/A	32.04 ± 0.67	31.49 ± 0.3	N/A	31.28 ± 0.67 31.79 ± 1.9
ClO_3	45.7 ± 0.4	N/A		44.3 ± 0.4	N/A	
$HClO_2$	6.2 ± 0.4	N/A		5.0 ± 0.4	N/A	[1.0][f]
$HClO_3$	−0.9 ± 0.3	N/A		−2.6 ± 0.3	N/A	[−4.2][f]
$HClO_4$	2.9 ± 1.0	N/A		−0.1 ± 1.0	N/A	[−1.5][f]

[a] From W4.4 theory: FO and ClO; from W4.2 theory: HO_2, H_2O_2, HOF, F_2O, and HOCl; from W4 theory: FO_2, F_2 O_2, Cl_2O, OClO, ClOO, Cl_2O_2 (via the average of two isodesmic reactions, see text), ClO_3 (via the isodesmic reaction, see text), $HClO_2$ (via the isodesmic reaction, see text); from W4lite theory: $HClO_3$ (estimated value, see text); from W2.2 theory: $HClO_4$ (improved SCF component, see text). [b] Reference 55. [c] HO_2 and H_2O_2 from ref 40; HOF from ref 82; ClO from ref 54; HOCl: −17.68 ± 0.03 from ref 83; −17.4 ± 1.4 from ref 54; Cl_2O_2 from ref 69; ClO_3 from ref 76. [d] HO_2 and H_2O_2 from ref 40; ClO and ClOO from ref 71; HOCl from ref 83; Cl_2O_2: 31.28 kcal/mol from ref 69, 31.79 from ref 71. [e] W4 values obtained at the experimental reference geometry of ref 58 are the following: 9.27 and 8.21 kcal/mol at 0 and 298 K, respectively (see text). [f] Group additivity estimates from ref 85.

The $\hat{T}_5$ contribution approximated as CCSDTQ(5)$_\Lambda$/PVDZno*d*−CCSDTQ/PVDZno*d* reaches a fairly hefty 0.27 kcal/mol. All in all, at the W4 level, we obtain a TAE_0 of 146.00 ± 0.16 kcal/mol. Using the ATcT atomic heats of formation at 0 K, we obtain $\Delta H^{\circ}_{f,0}[F_2O_2(g)] = 8.90 \pm 0.18$ kcal/mol. Using the CODATA heat content function for O_2 and F_2, and calculating that of F_2O_2 at the B3LYP/pc2 level of theory, we arrive at $\Delta H^{\circ}_{f,298}[F_2O_2(g)] = 7.84 \pm 0.18$ kcal/mol. The experimental heat of formation of F_2O_2 ($\Delta H^{\circ}_{f,298}[F_2O_2(g)] = 4.73 \pm 0.30$ kcal/mol) was derived by Kirshenbaum[56] nearly 60 years ago from bomb calorimetry measurements for the reaction $F_2O_2(l) \rightarrow O_2(g) + F_2(g)$ at 190 K. There, two assumptions were made by the authors: (a) the heat of vaporization was estimated from Trouton's rule and (b) the results at 190 K were converted to 298 K by assuming that the heat capacity at constant volume ΔC_v for the reaction is zero over the entire temperature range. Thirty years later Lyman[57] reevaluated the latter assumption and arrived at $\Delta H^{\circ}_{f,298}[F_2O_2(g)] = 4.58 \pm 0.2$ kcal/mol. This value was adopted by the NIST-JANAF[55] thermochemical tables as the standard heat of formation of F_2O_2 (with a larger uncertainty of 0.5 kcal/mol). The B3LYP/pc2 differences in heat capacity at constant volume between the reactant (F_2O_2) and the products (O_2 and F_2) at 190 and 298 K are 0.6 and −1.7 cal/mol. Taking the mean of these two values as the ΔC_v and converting Kirshenbaum's results to 298 K we arrive at $\Delta H^{\circ}_{f,298}[F_2O_2(g)] = 4.67 \pm 0.2$ kcal/mol. In any case, the experimental heat of formation is about 3.2 kcal/mol lower than our (full W4) theoretical value.

The significant deviation between the CCSD(T)/PVQZ and experimental geometries (vide supra) is expected to affect the TAE to some extent. Most of the change, nevertheless, will be confined to the SCF, valence CCSD, and (T) and to the inner-shell CCSD(T) components. Recalculating these contributions at the experimental geometry[58] the TAE_0 goes down by 0.37 to 145.63 kcal/mol, thus raising $\Delta H^{\circ}_{f,0}$ and $\Delta H^{\circ}_{f,298}$ to 9.27 and 8.21 kcal/mol, respectively, and further increasing the gap between theory and experiment.

G. Chlorine Oxides. ***1. ClO ($^1\Pi_{3/2}$).*** The W4 TAE_0 of monochlorine monoxide (63.30 kcal/mol) is 0.7 kcal/mol higher than that at the W2.2 level, where most of the difference (0.61 kcal/mol) comes from the $\hat{T}_4$ contribution. At the W4.4 level we obtain a TAE_0 of 63.40 ± 0.10 kcal/mol, which is in excellent agreement with the Gurvich[54] value of 63.43 ± 0.01 kcal/mol, itself based on a spectroscopic dissociation energy from Coxon and Ramsay.[59] The JANAF[55] value (63.4 ± 0.5 kcal/mol) has a much larger uncertainty.

2. Cl_2O ($^1A_1$). The TAE_0 of dichlorine monoxide at the W4 level (96.93 kcal/mol) is 0.35 kcal/mol higher than that at the W2.2 level, where most of the difference comes from the post-CCSD(T) contributions. The higher order triples contribution, $\hat{T}_3$-(T), amounts to −0.88 kcal/mol, the $\hat{T}_4$ contribution to 1.16 kcal/mol, and the $\hat{T}_5$ contribution to merely 0.04 kcal/mol. The W4 TAE_0 (96.93 ± 0.16 kcal/mol) is spot on the Gurvich[54] value (96.9 ± 2.4 kcal/mol) and on the upper edge of the JANAF[55] uncertainty interval (96.4 ± 0.5). The W4 $\Delta H^{\circ}_{f,298}[Cl_2O(g)] = 18.82 \pm 0.16$ kcal/mol slightly overestimates the experimental value of 18.7 ± 1.4 kcal/mol based on a photoionization mass spectrometric study.[60] Assuming that the energy of the $Cl_2O + H_2O \rightarrow 2HOCl$ isodesmic reaction stays the same at the W4 and W4.4 levels, the W4.4 TAE_0 is estimated to be 97.18 ± 0.27 kcal/mol. [We note that the enthalphy change (at the W4 level) of this reaction is only 2.87 kcal/mol.] This results in a W4.4 $\Delta H^{\circ}_{f,298}[Cl_2O(g)] = 18.57 \pm 0.27$ kcal/mol, slightly below the said experimental value.

3. OClO ($^2B_1$) and ClOO ($^2A''$). Both OClO and ClOO isomers are dominated by severe NDC effects (vide supra), the latter slightly more pronouncedly so. The TAE_0 of chlorine dioxide (OClO) at the W4 level (122.33 ± 0.16) is 0.81 kcal/mol higher than that at the W2.2 level. About 0.15 kcal of this difference results from using more elaborate basis sets for the extrapolation of the SCF, CCSD, and CCSD(T) contributions, while the rest comes from the post-CCSD(T) contributions: −1.28, 1.78, and 0.12 from the $\hat{T}_3$-(T), $\hat{T}_4$, and $\hat{T}_5$ contributions, respectively. The JANAF[55] TAE_0 (122.9 ± 1.9) is 0.6 higher

TABLE 10: Performance Statistics (kcal/mol) of Various Exchange-Correlation Functionals for the Halogen Oxides Considered in the Present Work[a,f]

class	functional	rmsd	MSD	MAD	rmsd[b]	rmsd[c]	max error
GGA	HCTH407	14.37	11.92	11.99	14.47	12.08	3.08 (F_2O_2)
	BLYP	17.20	14.00	14.18	18.73	14.20	38.5 (F_2O_2)
	BPW91	21.59	19.50	19.50	21.61	18.87	41.4 (F_2O_2)
	BP86	29.46	27.52	27.52	28.27	26.10	51.5 (F_2O_2)
	PBE	31.76	29.43	29.43	29.92	28.11	54.4 (F_2O_2)
meta GGA	M06-L	5.08	0.73	4.34	5.00	4.01	9.0 (F_2O_2)
	VSXC	7.02	−0.70	5.48	5.86	4.85	−16.1 ($HClO_4$)
	TPSS	11.23	8.41	9.14	12.26	8.99	26.1 ($F_2 O_2$)
	τHCTH	12.26	9.90	9.99	12.94	10.08	28.2 ($F_2 O_2$)
hybrid GGA	PBE0	2.68	−1.44	2.08	2.01	2.36	−6.2 ($HClO_4$)
	B97-2	2.92	0.56	2.59	2.58	2.34	−5.7 ($HClO_4$)
	B3PW91	3.31	−0.74	2.60	2.10	2.35	−9.1 ($HClO_4$)
	B97-1	4.64	2.21	3.80	4.58	3.53	8.2 ($F_2 O_2$)
	B98	4.65	−0.98	3.36	2.26	3.11	−13.6 ($HClO_4$)
	TPSSh	6.61	−2.23	4.67	3.09	4.45	−19.4 ($HClO_4$)
	B3LYP	7.46	−3.94	4.99	3.07	5.51	−21.6 ($HClO_4$)
hybrid meta GGA	mPW1K	27.57	−25.51	25.51	24.17	24.53	−43.8 ($HClO_4$)
	BHLYP	44.71	−41.09	41.09	37.41	39.19	−77.0 ($HClO_4$)
	mPW28B95	2.55	1.99	2.23	2.72	2.52	3.9 ($Cl_2 O_2$)
	mPW1B95	2.53	−1.33	1.91	1.68	1.94	−6.2 ($HClO_4$)
	B1B95	2.78	−1.18	1.92	1.42	2.06	−7.9 ($HClO_4$)
	M06	3.27	−2.73	2.77	2.86	2.87	−6.0 ($HClO_4$)
	PW6B95	4.16	−2.47	2.91	1.80	3.05	−11.9 ($HClO_4$)
	TPSS1KCIS	5.29	−0.24	4.03	3.53	3.42	−14.4 ($HClO_4$)
	M05	5.51	−4.37	4.56	6.05	5.39	−10.6 (FO_2)
	τHCTHh	6.64	4.73	5.38	7.22	5.36	14.7 ($F_2 O_2$)
	BMK	8.65	−6.48	6.48	5.24	7.09	−19.9 ($HClO_4$)
	M06−2X	8.08	−6.15	6.16	5.81	6.73	−15.7 ($HClO_4$)
	BB1K	17.27	−15.67	15.67	14.85	14.92	−28.6 ($F_2 O_2$)
	PWB6K	21.62	−19.72	19.72	19.18	18.58	−34.5 ($F_2 O_2$)
double hybrid	B2-PLYP[d]	3.01	−0.61	2.17	1.73	1.84	−9.1 ($HClO_4$)
	B2-PLYP[e]	1.85	0.14	1.51	1.76	1.73	4.0 (OClO)
	B2GP-PLYP[d]	4.62	−3.92	3.92	3.41	3.49	−10.5 ($HClO_4$)
	B2GP-PLYP[e]	4.28	−3.54	3.64	4.59	3.28	−8.1 (F_2O_2)
	B2T-PLYP[d]	5.07	−4.18	4.18	3.25	3.81	−12.7 ($HClO_4$)
	B2T-PLYP[e]	4.14	−3.60	3.66	4.15	3.20	−6.9 (F_2O_2)
	B2K-PLYP[d]	6.21	−5.58	5.58	5.43	4.99	−10.8 ($HClO_4$)
	B2K-PLYP[e]	6.37	−5.43	5.43	6.88	5.05	−12.9 (F_2O_2)
	mPW2-PLYP[d]	5.49	−4.43	4.43	3.23	4.18	−14.1 ($HClO_4$)
	mPW2-PLYP[e]	4.04	−3.55	3.55	3.77	3.14	−7.2 ($HClO_4$)

[a] HOF, F_2O, FO, FO_2, F_2O_2, ClO, Cl_2O, OClO, ClOO, Cl_2O_2, HOCl, ClO_3, $HClO_2$, $HClO_3$, and $HClO_4$. [b] Excluding the pseudohypervalent systems ClO_3, $HClO_3$, and $HClO_4$. [c] Excluding ClOO, $HClO_4$, and F_2O_2. [d] aug′-pc2+2d basis set combined with a CBS extrapolation where Nmin = 10 as recommended in ref 134. [e] aug′-pc3+d basis set combined with a CBS extrapolation where Nmin = 15 as recommended in ref 134. [f] Unless otherwise indicated all calculations were done with the aug-pc2’+2d basis set.

than the W4 value. The W4.2, W4.3, and W4.4 TAE_0 are estimated to be 122.34, 122.48, and 122.47 kcal/mol by assuming that the energy of the OClO + H_2O → HOO + HOCl reaction stays the same at the W4 and post-W4 levels. A few experimental heats of formation are available: $\Delta H^{\circ}_{f,0}$[OClO(g)] = 24.12 ± 0.24[61] and 23.7 ± 1[62] kcal/mol, $\Delta H^{\circ}_{f,298}$[OClO(g)] = 23.53 ± 0.24,[61] 23.1 ± 1,[62] and 23 ± 2[63] kcal/mol. The W4 heats of formation at 0 and 298 K, 24.26 ± 0.16 and 23.67 ± 0.16 kcal/mol, are in good agreement with those of Davis.[61] The Gurvich[54] value of $\Delta H^{\circ}_{f,298}$[OClO(g)] = 25.1 ± 1.4 kcal/mol, from an average of 1920s and 1930s era calorimetric measurements, is hard to reconcile both with our calculated value and with more recent experiments. The available experimental D°_0[O−ClO] values are 59.0 ± 0.2,[61] 59.1 ± 0.1,[64] and 59.3 ± 0.5[65] kcal/mol, the former two values being in good agreement with our W4 value of 59.03 ± 0.23 kcal/mol.

For the chlorine superoxide isomer (ClOO), similar to the FOO case, the relativistic basis-set limit CCSD(T) TAE_0 at the W2.2 level is about 3.5 kcal/mol lower than the W4 TAE_0. At the W4 level the $\hat{T}_4$ contribution amounts to as much as 3.14 kcal/mol and the higher order triples, $\hat{T}_3$-(T), contribution to 0.11 kcal/mol. Thus, similarly to FO and ClO, there is mutual amplification, rather than cancelation, between the connected quadruples and the higher order triples contributions. The connected quintuple excitations, $\hat{T}_5$, calculated with the PVDZn-o*d* basis set further increase the TAE by 0.22 kcal/mol. The W4 TAE_0 (121.88 ± 0.32 kcal/mol) is lower by 0.8 kcal/mol than the JANAF[55] value (122.7 ± 1.0 kcal/mol): we note that the uncertainty of the W4 value was arbitrarily doubled in light of the very large post-CCSD(T) contributions. At the W4 level the OClO isomer is more stable than ClOO by 0.44 kcal/mol, in agreement with the experimental enthalpy of isomerization of Davis[61] (0.3 ± 0.25 kcal/mol). The available experimental Cl−OO bond dissociation energies at 0 K are the following: 4.76 ± 0.5,[66] 4.83 ± 0.05,[67] and 4.6 ± 0.4[68] kcal/mol. At the W4 level we obtain D°_0 = 4.0 kcal/mol.

4. Cl_2O_2 (^1A). According to our diagnostics (Table 1) chlorine peroxide is dominated by severe NDC effects, albeit to a lesser extent than F_2O_2. The W2.2 TAE_0 is 142.0 kcal/mol. Using more elaborate basis sets for the extrapolation of the SCF, CCSD, and CCSD(T) contributions raises the TAE by 0.1 kcal/mol. The higher order connected triples, $\hat{T}_3$-(T), contribution is −1.3

kcal/mol, and the parenthetical quadruples contribution is 1.8 kcal/mol, hence at the W4lite level we obtain a TAE_0 of 142.65 ± 0.26 kcal/mol.

In Cl_2O_2 the O−O bond length is 0.05 Å shorter than that in H_2O_2, and the Cl−O bond length is ~0.02 Å longer than that in Cl_2O and HOCl. Thus, the W4 TAE_0 can be reliably estimated by means of isodesmic reactions involving these species. In contrast, in the F_2O_2 case we choose not to follow this strategy (and thus carry out the strenuous W4 calculations) since the O−O bond length is 0.2 Å shorter than the corresponding bond in H_2O_2, and the F−O bond length is at least 0.1 Å longer than the corresponding bond in F_2O, HOF, or OF. Two possible isodesmic reactions come to mind: $Cl_2O_2 + H_2O \rightarrow H_2O_2 + Cl_2O$ and $Cl_2O_2 + 2HOCl \rightarrow H_2O_2 + 2Cl_2O$. Assuming that the W4lite and W4 reaction energies are the same, and assuming the uncertainty in the reaction energy would be no greater than that for an individual TAE, we obtain TAE_0 values of 142.89 ± 0.4 and 142.94 ± 0.5 kcal/mol, respectively. Averaging the two, we get 142.9 ± 0.3 kcal/mol.

Combining this with the ATcT atomic heats of formation and correcting for thermal terms we obtain $\Delta H^{\circ}_{f,0}[Cl_2O_2(g)] = 32.3 \pm 0.3$ and $\Delta H^{\circ}_{f,298}[Cl_2O_2(g)] = 31.5 \pm 0.3$ kcal/mol, in reasonable agreement with the recently reported experimental values of 32.04 ± 0.67 and 31.28 ± 0.67 kcal/mol, respectively, that were deduced from a photoionization mass spectrometry study.[69] Earlier determinations of $\Delta H^{\circ}_{f,298}[Cl_2O_2(g)]$ include 30.5 ± 0.7[70] and 31.8 ± 1.9[71] kcal/mol. In addition a number of experimental determinations of the ClO−OCl bond strength are available at 0 K (15.87 ± 0.7[72] and 16.25 ± 0.67[69] kcal/mol) and at 298 K (17.3 ± 0.67,[69] 19.5 ± 0.7,[73] 17.3 ± 0.7,[74] and 16.5 ± 0.7[75] kcal/mol). At the W4 level we obtain $D^{\circ}_{0}[ClO-OCl] = 16.3 \pm 0.4$ and $D^{\circ}_{298}[ClO-OCl] = 17.1 \pm 0.4$ kcal/mol.

5. ClO_3 ($^2A_1$). The W3.2 TAE_0 (159.68) is 0.67 kcal/mol higher than that at the W2.2 level. Using more elaborate basis sets for the extrapolation of the SCF, CCSD, and CCSD(T) contributions in W4lite theory further increases the TAE_0 by 0.4 to 160.08 kcal/mol. Of the possible isodesmic reactions at our disposal, the $ClO_3 + ClO \rightarrow 2OClO$ reaction offers the smallest variation in the Cl−O bond lengths between the reactants and products. Employing this reaction, and assuming the uncertainty in the reaction energy would be no greater than that for an individual TAE, we obtain an estimated W4 TAE_0 of 159.9 ± 0.4 kcal/mol. Using this value we arrive at $\Delta H^{\circ}_{f,0}[ClO_3(g)]$ and $\Delta H^{\circ}_{f,298}[ClO_3(g)]$ of 45.7 and 44.3 kcal/mol, respectively. Colussi[76] obtained a $\Delta H^{\circ}_{f,0}[ClO_3(g)]$ of 55.6 ± 4 kcal/mol from low-pressure rate coefficients for the O + OClO → ClO_3 reaction.

H. Hydrides. As noted above (Section III.A), of the species studied in this work, the hydrides are the simplest from the electronic structure point of view. These systems exhibit comparatively milder NDC effects: %TAE[(T)] diagnostics are typically about half those of the halogen oxides (Table 1). Thus, even W2.2 theory can provide somewhat useful results, which is particularly relevant to the larger hydrides ($HClO_3$ and $HClO_4$) where W4 theory is currently not a viable option.

1. HO_2 ($^2A''$) and H_2O_2 (^1A). At the W4 level $\hat{T}_3$-(T) corrections to the TAEs are −0.17 and −0.55 kcal/mol for HO_2 and H_2O_2, respectively, while the $\hat{T}_4$ contributions are 0.65 and 0.72 kcal/mol, respectively (Table 7). The W4.2 TAE_0, which are only nominally different from the W4 values, are 165.97 ± 0.14 and 252.08 ± 0.14 kcal/mol, respectively. (This is quite close to the best HEAT values,[80] 166.04 and 252.01 kcal/mol, respectively.) The TAE_0 of HO_2 is spot on the ATcT value (165.98 ± 0.05)[40] and is also in very good agreement with several recent high-quality theoretical TAE_0 values, 166.0 ± 0.3 kcal/mol (Feller and Peterson),[77] 166.0 ± 0.18 kcal/mol (HEAT),[78] and 166.0 ± 0.15 kcal/mol (Flowers).[81] The ATcT TAE_0 for hydrogen peroxide[80] (252.21 ± 0.02 kcal/mol) lies at the upper end of the W4.2 uncertainty interval. By assuming that the energy of the $2H_2O_2 \rightarrow O_2 + 2H_2O$ reaction stays constant at the W4.2 and post-W4.2 levels, the W4.3 and W4.4 TAE_0 of H_2O_2 are estimated to be 252.13 and 252.05 kcal/mol, respectively.

2. HOF ($^1A'$). At the W4 level the $\hat{T}_3$-(T), $\hat{T}_4$, and $\hat{T}_5$ contributions to the TAE amount to −0.41, 0.72, and 0.04 kcal/mol, respectively (Table 7). The W4.2 TAE_0 (149.24 ± 0.16 kcal/mol) overshoots the ATcT value (148.96 ± 0.15 kcal/mol, quoted in ref 77) by 0.28 kcal/mol, which is still within overlapping uncertainties. Utilizing the W4.4 atomization energies for HOF, H_2O, and FO and the W4.2 reaction for the isodesmic reaction, HOF + OH → FO + H_2O, the W4.4 TAE_0 of HOF is estimated to be 149.33 kcal/mol, further increasing the gap between theory and experiment. For comparison, the best theoretical estimate of Feller and Peterson[77] is 149.1 ± 0.3 kcal/mol.

At the W4.2 level we obtain $\Delta H^{\circ}_{f,0}[HOF(g)] = -20.15$ kcal/mol, which can be compared to the suggested revised experimental enthalpy of formation at 0 K of Peterson and co-workers, −20.02 ± 0.25 kcal/mol.[82]

3. HOCl ($^1A'$). As mentioned in Section III.D, the $\hat{T}_3$-(T) contribution to the TAE_0 at the W4 level (−0.47 kcal/mol) is overestimated by 0.36 kcal/mol relative to the contribution at the W4.3 level. The W4 $\hat{T}_4$ and $\hat{T}_5$ contributions amount to 0.58 and 0.02 kcal/mol, respectively. The W4.2 TAE_0 (156.73 ± 0.14 kcal/mol) is 0.4 kcal/mol higher than the JANAF[55] TAE_0 (156.3 ± 0.5 kcal/mol) and 0.1 kcal/mol higher than the Gurvich[54] value (156.6 ± 1.2 kcal/mol). The W4.4 TAE_0 can be estimated by means of the HOCl + OH → OCl + H_2O isodesmic reaction; assuming that the W4.2 − W4.4 difference leaves the reaction energy unchanged, we obtain a TAE_0 of 156.81 ± 0.22 kcal/mol, to be compared to the ATcT value[20] of 156.64 ± 0.43 kcal/mol. Combining our calculated TAE_0 and the ATcT atomic heats of formation at 0 K, we obtain $\Delta H^{\circ}_{f,0}[HOCl(g)] = -17.51 \pm 0.14$ kcal/mol at the W4.2 level, and an estimated W4.4 value of −17.59 ± 0.22 kcal/mol. Converting these to 298 K using the CODATA heat content function for H_2, O_2, Cl_2 and HOCl we arrive at $\Delta H^{\circ}_{f,298}[HOCl(g)] = -18.20 \pm 0.14$ and −18.28 ± 0.22 kcal/mol at the W4.2 and W4.4 levels, respectively. Our heats of formation at the W4.4 level are in line with the experimental values of Joens,[83] $\Delta H^{\circ}_{f,0}[HOCl(g)] = -17.68 \pm 0.03$ and $\Delta H^{\circ}_{f,298}[HOCl(g)] = -18.36 \pm 0.03$ kcal/mol, determined from the measurement of the Cl−OH bond energy.

4. $HClO_2$ (^1A). The equilibrium geometry of chlorous acid has no symmetry: for this reason we were only able to obtain a W4lite value for this system. At the W2.2 level, the internal rotation barrier is 3.60 kcal/mol, which we judged too large to remain unchanged from W2.2 to W4 (cfr. next section). The W3.2 TAE_0 (192.05 kcal/mol) is 0.61 kcal/mol higher than at the W2.2 level. Higher order triples, $\hat{T}_3$-(T), and parenthetical quadruples (Q) contributions amount to −0.91 and 1.52 kcal/mol, respectively. Improving the extrapolations for the SCF, CCSD, and (T) components in W4lite raises the TAE_0 to 192.11 ± 0.3 kcal/mol. Using the HOClO + ClO → HOCl + OClO isodesmic reaction, and assuming that the uncertainty on the W3.2 reaction energy would be no greater than that for an individual computed TAE at that level (0.26 kcal/mol), we obtain a W4 estimate for the TAE_0 of 192.0 ± 0.4 kcal/mol. This results in $\Delta H^{\circ}_{f,0}[HClO_2(g)]$ and $\Delta H^{\circ}_{f,298}[HClO_2(g)]$ of 6.21

± 0.4 and 4.96 ± 0.4 kcal/mol, respectively. Two [somewhat uncertain] experimental determinations are available: McGrath[84] reported an experimental $\Delta H^o_{f,0}$[$HClO_2$(g)] of 8 ± 4 and Colussi and Grela,[85] based on a group additivity estimate, derived $\Delta H^o_{f,298}$[$HClO_2$(g)] = 1.0 kcal/mol.

5. $HClO_3$ (^1A). The ground state of chloric acid has no symmetry, thus, we were only able to carry out a W2.2 calculation on this system. The W2.2 TAE_e is 269.94 kcal/mol. Extrapolating the SCF component from the aug-cc-pV{5,6}+2d1f basis set pair results in a TAE_e of 270.33 kcal/mol. We note that at the W2.2 level (with an improved SCF component) the zero-point exclusive barrier for internal rotation about the Cl−OH bond is only 0.37 kcal/mol. (The barriers at the SCF, valence CCSD, and valence CCSD(T) limits are −0.57, +0.19, and 0.36 kcal/mol, respectively.) It is reasonable to assume that this barrier would not vary significantly upon further improvement of the electron correlation treatment, as post-CCSD(T) contributions will be roughly the same in the ground state and in the transition state. We therefore resorted to calculating the TAE_e of this transition state, which has C_s symmetry, at the W4lite level and estimating the W4lite − W2.2 difference for the $HClO_3$ ground state from the internal rotation barrier at the W2.2 level. The W4lite TAE_e of the $HClO_3$ transition state is 270.46 ± 0.26 kcal/mol. The uncertainty in the internal rotation barrier is somewhat hard to quantify, but 0.15 kcal/mol would appear to be a conservative estimate. Thus, the estimated W4lite TAE_e for the $HClO_3$ ground state is 270.83 ± 0.3 kcal/mol, which is almost 1 kcal/mol above the W2.2 value. Inclusion of the ZPVE from a B3LYP/aug-pc2+2d quartic force field calculation (12.78 kcal/mol) results in a W4lite TAE_0 of 258.05 ± 0.3 kcal/mol.

6. $HClO_4$ ($^1A'$). Perchloric acid was recently studied by one of us at the W1w and W2w levels.[53] The crucial importance of tight *d* functions in the basis set for the convergence of the SCF component was stressed as these functions improve the ability of the Cl 3d Rydberg orbital to act as an acceptor for backbonding from the oxygen lone pair orbitals: $HClO_4$ and Cl_2O_7, both involving Cl(VII), are so far the most extreme examples described.[53] The main difference between that study and the present one is the reference geometry used: here we use a CCSD(T)/PVQZ optimized geometry, while there a reference geometry optimized at the B97-1/aug-pc-3+d level of theory was employed. The main difference between the two geometries lies in the Cl−OH bond, which is 0.02 Å longer (and in fact fortuitously closer to experiment) in the DFT geometry. We note that the SCF and correlation components of TAE individually will change quite a bit between the two geometries, but most of the changes will mutually cancel.

Extrapolating the SCF component from the aug-cc-pV{5,6}Z+2d1f basis set pair using the Karton−Martin[32] extrapolation formula we obtain 80.55 kcal/mol. For the CCSD component, we obtain 227.42 kcal/mol, and for the (T) contribution 26.46 kcal/mol. The DBOC contribution, which is not included in W2w, amounts to 0.11 kcal/mol. All in all, we obtain at the W2.2 level (with an improved SCF component) a TAE_0 of 313.35 ± 1.7 kcal/mol, compared to 313.68 kcal/mol obtained in ref 53. Using the heat content function ($H_{298} - H_0$) from ref 53 results in $\Delta H^o_{f,0}$[$HClO_4$(g)] and $\Delta H^o_{f,298}$[$HClO_4$(g)] of 2.86 ± 1.7 and −0.10 ± 1.7 kcal/mol, respectively. This latter uncertainty should be considered very conservative, as the very low %TAE[(T)] diagnostic (2.28%, the lowest of all species considered in the present paper) suggests very small contributions from post-CCSD(T) correlation effects. If N_2O, NO_2, and O_3 are removed from the W4 set as intrinsically having too strong NDC for W2.2 to be applicable to them (as in the original W1 and W2 paper),[42] then the rmsd for W2.2 drops from 0.85 to 0.36 kcal/mol. Arbitrarily adjusting this number upward for the remaining uncertainty arising from problematic basis set convergence in this system, we suggest ±1 kcal/mol as a plausible error bar.

I. Theoretical vs Experimental Heats of Formation. Calculated and experimental heats of formation are summarized in Table 9. The following general statements can be made.

For many of the species (HO_2, HOF, FO, F_2O, FO_2, ClO, HOCl, Cl_2O, OClO, Cl_2O_2, ClOO), theoretical and experimental heats of formation agree to within overlapping uncertainties. Among these, the computed numbers for FO, F_2O, FO_2, OClO, Cl_2O, ClOO, and to a lesser extent Cl_2O_2 carry considerably smaller uncertainties than their experimental counterparts.

For hydrogen peroxide, a small gap separates the uncertainty intervals of the theoretical and experimental numbers. As this molecule is relatively straightforward from an electronic structure point of view, and the ATcT value carries a very small uncertainty, this leaves the somewhat problematic zero-point vibrational energy of this molecule as the prime suspect.

For three of the remaining species, the only available "experimental" values are crude group additivity estimates,[85] which agree as well (or poorly) with our calculations as one can expect.

This leaves FOOF and ClO_3 with large discrepancies between theory and experiment. As the discrepancies are an order of magnitude larger than the expected uncertainly of the calculations, it can safely be concluded that the measured values are in error.

J. DFT Functionals. Finally, it is of interest to compare the relative performance of different DFT exchange-correlation functionals in predicting the binding energies of the 15 halogen oxides considered in the present work. Halogen oxides were the subject of numerous DFT investigations (see for example refs 17, 13, 11, 53, 86, 87 and references cited therein) and are considered a challenging test case for DFT functionals. So far nearly all of the studies that evaluated the performance of DFT functionals used reference data at the CCSD(T) or MP2 level which we have clearly shown to be inadequate in describing most of the halogen oxides considered here.

As benchmark data we used our best available nonrelativistic, clamped-nuclei, zero-point exclusive TAEs (namely, W2.2 for $HClO_4$; W4lite for Cl_2O_2, ClO_3, $HClO_2$, and $HClO_3$; and W4 for all the rest). The exchange-correlation functionals employed range from generalized gradient approximation (GGA) [HCTH407,[88] BLYP,[89,90] BPW91,[89,91] BP86,[89,92] and PBE[93]] to meta-GGA [M06-L,[94] VSXC,[95] TPSS,[96] and τ -HCTH[97]], hybrid-GGA [PBE0,[98] B97-2,[99] B3PW91,[91,100] B97-1,[101] B98,[102] TPSSh,[103] B3LYP,[90,100,104] mPW1K,[105] and BHLYP[106]], hybrid-meta-GGA [mPW28B95,[109] mPW1B95,[110] B1B95,[89,108] M06,[111] PW6B95,[112] TPSS1KCIS,[113] M05,[114] τ-HCTHh,[97] BMK,[115] M06-2X,[111] BB1K,[116] and PWB6K[112]], and double hybrid functionals [B2-PLYP,[117] mPW2-PLYP,[118] B2T-PLYP,[119] B2K-PLYP,[119] and B2GP-PLYP[120]]. Unless otherwise indicated, the aug-pc2+2d basis set of Jensen was used. The CCSD(T)/PVQZ reference geometries, the reference TAEs, and the results of the various functionals can be found in the Supporting Information. The rmsd, MSD, and MAD are gathered in Table 10.

Three general observations can be made. First, the GGA functionals systematically and substantially overestimate the binding energies and lead to rmsds of 14−32 kcal/mol. Second, of the pure DFT functionals considered, only the M06L meta-GGA performs acceptably for the thermochemistry of these species, with an overall rmsd of 5.1 kcal/mol. Third, the "kinetics" functionals considered (mPW1K, PWB6K, BB1K, BMK, and M06-2X) systematically underestimate the binding energies and lead to unacceptable rmsds of 9−28 kcal/mol.

A few specific remarks are in order. First, the FOOF molecule (as documented previously)[13] is a tough test for any DFT functional. Second, with some "kinetics-friendly" (i.e., high exact exchange) functionals (notably BB1K and M06-2X), the Kohn−Sham equations for ClOO exhibit two solutions, one a relatively pure doublet, and another with significant quartet contamination. For M06-2X, the latter solution is no less than 40 kcal/mol more stable (and closer to the reference value) than the former. Not surprisingly, similar phenomena are seen with the double hybrids: however, at the B2GP-PLYP level, the two solutions are nearly degenerate in energy once the MP2-like component is put in. (At the B2-PLYP and B2K-PLYP levels, the "pure" and "contaminated" solutions are about 1 kcal/mol apart once the MP2-like correlation term is put in.)

Considering the overall rmsd of the hybrid GGAs, PBE0 and B97-2 put in the best performance (2.9 kcal/mol), followed by B3PW91 (3.3 kcal/mol), B97-1 (4.6 kcal/mol), and B98 (4.7 kcal/mol). The hybrid GGAs tend to severely underbind the pseudohypervalent systems $HClO_3$, ClO_3, and $HClO_4$; upon exclusion of these molecules, PBE0, B3PW91, B98, and B97-2 emerge as the best performers, with rmsd of 2.0, 2.1, 2.3, and 2.6 kcal/mol, respectively. TPSSh and B3LYP tie for fifth place with a rmsd of 3.1 kcal/mol.

Among the "pure DFT" functionals, the M06L and VSXC meta-GGAs put in the best and second best performance, respectively. At the other end, all "kinetics friendly" high-HF exchange hybrids except M06-2X and BMK perform poorly.

It can be noted that B3PW91 (and, indeed, B1B95) perform appreciably better than B3LYP. For the most part, this reflects the poor performance of the LYP correlation functional for the pseudohypervalent compounds (see also ref 120).

Several hybrid meta-GGAs do quite well, most notably the nonstandard hybrid mPW1B95 functional (2.5 kcal/mol), followed by mPW28B95 (2.6 kcal/mol), B1B95 (2.8 kcal/mol), and M06 (3.3 kcal/mol). Excluding the pseudohypervalent systems, B1B95, mPW1B95, and PW6B95 show the best performance, with rmsds of 1.4, 1.7, and 1.8 kcal/mol, respectively.

The B2GP-PLYP, B2T-PLYP and B2K-PLYP double hybrids systematically underestimate the molecular binding energies and lead to rmsds larger than 4 kcal/mol, i.e., more than twice the overall rmsd of these functionals for the atomization energies in the W4-08 set.[120] B2-PLYP, however, performs exceptionally well for all the halogen/hydrogen oxides considered, with an overall rmsd under 2 kcal/mol with the aug′-pc3+d basis set. This is due to an error compensation with oversaturation in MP2-type correlation, as B2-PLYP was parametrized for a relatively small basis set (see ref 120 for more details). For the mPW2-PLYP double hybrid,[118] which was parametrized by using a larger basis set, we again find an underestimate. Note also (Table 10) that error statistics for all double hybrids are considerably improved if ClOO, F_2O_2, and $HClO_4$ are excluded. While the double hybrids go a long way in remedying the weakness of the LYP correlation functional for pseudohypervalent systems, it is not removed entirely. (It was previously shown[117,120] that for general thermochemistry, the LYP correlation functional clearly outperforms all others in a double-hybrid context, while the choice of exchange functional appears to be much less critical.)

Considering only the pseudohypervalent systems ($HClO_3$, ClO_3, and $HClO_4$) the hybrid meta-GGA functionals mPW28B95 and M05 give the best performance with a rmsd of 1.7 and 2.3 kcal/mol, and the double hybrids B2-PLYP and B2GP-PLYP with a rmsd of 2.2 and 2.7 kcal/mol. If, on the other extreme, one considers only the systems which exhibit pathological multireference character (defined here as systems with $\%TAE_e[(T)] \geq 10\%$, i.e., FO, F_2O, FO_2, F_2O_2, ClO, Cl_2O, ClOO, OClO, and Cl_2O_2), then B1B95 and PBE0 offer the best performance with a remarkably low rmsd of 1.2 kcal/mol, followed by PW6B95, mPW1B95, B2-PLYP, and B3PW91 with rmsds of 1.6, 1.7, 1.7, and 2.1 kcal/mol, respectively.

IV. Conclusions

Benchmark-quality W4 (and related) thermochemical data were obtained for the fluorine and chlorine oxides and some related hydrides, all of which are of interest for computational modeling of atmospheric processes. Our best available estimates (in kcal/mol) for total atomization energies at 0 K are the following: HO_2 165.97 ± 0.14, H_2O_2 252.08 ± 0.14, HOF 149.24 ± 0.14, FO 51.17 ± 0.10, F_2O 89.43 ± 0.14, FO_2 130.15 ± 0.16, F_2O_2 146.00 ± 0.16, ClO 63.40 ± 0.10, HOCl 156.73 ± 0.14, Cl_2O 96.93 ± 0.16, OClO 122.33 ± 0.16, ClOO 121.88 ± 0.32, Cl_2O_2 142.9 ± 0.3, ClO_3 159.9 ± 0.4, $HClO_2$ 192.0 ± 0.4, $HClO_3$ 258.1 ± 0.3, and $HClO_4$ 313.4 ± 1. For several of these species, the total atomization energy contains unusually large components from correlation effects beyond CCSD(T). The geometry of FOOF is significantly affected by connected quadruple excitations. The fluorine and chlorine oxides are particularly demanding systems for density functional methods, and several observations about their performance for these systems have been made.

Supporting Information Available: Optimized Cartesian coordinates of all the species studied, CCSD(T)/cc-pV(Q+d)Z harmonic frequencies for some species, and detailed results of the various DFT functionals along with the reference TAEs used. This material is available free of charge via the Internet at http://pubs.acs.org.

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