DFT and *Ab Initio* Composite Methods: Investigation of Oxygen Fluoride Species

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ABSTRACT

The capability of ccCA, G3, and G3B3 for the prediction of the enthalpies of formation of oxygen fluoride species was evaluated. In addition to these composite methods, the performance of M06 and M06-2X in conjunction with the correlation consistent basis sets (aug-cc-pVnZ), where $n = D, T, Q$, was also examined for predicting the structures and enthalpies of formation of oxygen fluoride species. A set of various oxygen fluorides were considered, including FO_x radicals, FO_xH, and FO_xF, where $x = 1-3$. The effects of basis set size and spin contamination were also considered.

KEYWORDS

oxygen fluorides
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1. INTRODUCTION

The oxygen fluorides have attracted interest because they can be employed as propellants in the rocket industry and can be used as strong fluorinating and oxidizing agents. In addition, oxygen fluorides play a role as intermediates in atmospheric chemistry and are believed to make a minor contribution to the destruction of ozone [1–6]. The source of fluorine in the atmosphere originates from the decomposition of chlorofluorocarbons (CFCs) and their radical fragments, but most of the atmospheric fluorine is in the form of hydrogen fluoride (HF). Hydrogen fluoride is formed from the fast reaction of a fluorine atom with methane and water vapor [5,7]. Although the role of fluorine in ozone depletion is minor, the percentage of fluorine in the atmosphere has been reported to be increasing with time [8–10]. Thus, accurate thermochemical properties are required for modeling fluorine compounds in the study of atmospheric reactions. Due to the unstable nature of oxygen fluorides, experimental measurements of the energetic properties have been limited. Computational approaches can aid in understanding such systems.

Investigating the structural properties of the oxygen fluorides has been a challenge to the computational chemical community, particularly for FOO and FOOF. The F-O bond in oxygen fluorides is a covalent bond between two highly electronegative atoms where both atoms contain lone pair electrons. Therefore, the F-O bond exhibits strong electron lone pair – lone pair repulsion and can become very long in molecules such as FOO and FOOF (~ 0.2 Å longer than the F-O bond in FOF) [11,12], requiring consideration of high-level electron correlation methods. In FOO and FOOF, the O-O bond length is similar to that in the O₂ molecule but ~ 0.2 Å shorter than the O-O bond length in HOOH [11]. The unusual geometry of FOO and FOOF presented a computational difficulty for electronic structure methods, which led to numerous investigations of oxygen fluorides using a variety of methods to study their structures and energetic properties [13–30]. Many methods have been unsuccessful in predicting the right structure for oxygen fluorides, such as FOO, FOOO, and FOOF, with respect to the experimental geometries, as will be seen in the following sections.

As a full literature review of these efforts is outside the scope of this paper, a number of significant and recent investigations are highlighted. The FOO structure and enthalpy of formation ($\Delta H^\circ_{f, 298}$) have been computed by Francisco *et al.* [16] using Møller-Plesset perturbation theory (MP2, MP3, and MP4), complete active space self-consistent field (CASSCF), and quadratic configuration interaction [QCISD(T)] in conjunction with Pople’s basis sets. The study found that all MP n methods underestimated the FO bond length by > 0.2 Å. QCISD(T)/6-31G(d) yielded the best FO bond length that is only shorter by 0.002 Å from the experimental length (expt. r_e (F-O) = 1.649 ± 0.013 Å [31], where r_e indicates an equilibrium structure), whereas the best CASSCF description of the F-O bond length is 0.8 Å shorter than experiment. Francisco’s study reported an enthalpy of formation at 0 K for FOO of 8.9 ± 3 kcal mol⁻¹ by using isodesmic and isogyric reaction schemes using QCISD(T)/6-311G(d,p) results [16]. Ventura and Kieninger’s [26] study on FOO concluded that B3LYP/6-311++G(3df, 3pd) is a reliable method to describe structures and predict reaction enthalpies for molecules involving F-O bonds. Studies by Denis [30,32,33] found that the inclusion of the full treatment of the triple excitation [CCSDT instead of CCSD(T)] overcame the spin contamination problem presented in UCCSD(T), hence CCSDT predicted an accurate structure and energetics of the FOO molecule. Karton *et al.*, [20] reported the $\Delta H^\circ_{f, 298}$ of FOO of 5.87 ± 0.16 kcal mol⁻¹ in excellent agreement with experiment (6.1 ± 0.5 kcal mol⁻¹) using the high-level computationally demanding W4 method [34]. A recent theoretical study by Feller *et al.* [15] obtained a correct structure of FOO using R/UCCSD(T)/aug-cc-pVTZ level of theory and with a calculated value of $\Delta H^\circ_{f, 298}$ of 6.4 ± 0.7 kcal mol⁻¹ using a composite approach that is based on coupled cluster theory with up to quadruple excitations. The difference in the uncertainties estimated by Karton’s (5.87 ± 0.16 kcal mol⁻¹ [20]) and Feller (6.4 ± 0.7 kcal mol⁻¹ [15]) imputes to their different approaches. While W4 estimates uncertainties based on the performance of a set of 25 small molecules [20], Feller’s approach uses molecule-by-molecule criteria to calculate the estimated uncertainties [15].

The structure and the $\Delta H^\circ_{f, 298}$ of FOOF have been studied extensively with a broad variety of quantum chemical methods. The computational challenge in the FOOF structure arises from the anomeric delocalization effect that exists in FOOF between the oxygen lone pair and the antibonding orbital of the F-O bond [29]. Although CCSD(T)/aug-cc-pVTZ [15] and B3LYP/6-311++G(2d) [18] can provide a qualitatively correct geometry for FOOF, very few methods used in previous work reproduced the experimental FOOF structure. In fact, a local density functional (LDF) paired with numerical and Gaussian basis sets [35] and the local

SVWN functional paired with 6-311++G(2d) [18] were two methods that predicted the closest r_e of the F-O bond compared to experiment, with LDF being superior. LDF predicted F-O and O-O bond lengths that are 0.01 Å and 0.001 Å off from experimental geometries ($r_s(\text{F-O}) = 1.575 \pm 0.003$ Å and $r_s(\text{O-O}) = 1.217 \pm 0.003$ Å [11]), respectively. LDF predicted this good description for FOOF likely due to the high and evenly distributed electron density in FOOF, as justified in Ref. 34. MP2, MP3, and MP4 with different size and type of basis sets, on the other hand, predicted incorrect geometries for FOOF with respect to experiment, however MP6 at the complete basis set (CBS) limit predicted an accurate geometry [29]. Not only is the structure of FOOF problematic but its $\Delta H_{f,298}^\circ$ has also been difficult to predict. The calculated $\Delta H_{f,298}^\circ$ of FOOF using even high-level *ab initio* methods has a large deviation from the experimental value reported in the NIST-JANAF thermochemical table (4.6 ± 0.5 kcal mol⁻¹) [36,37]. The $\Delta H_{f,298}^\circ$'s reported by Karton et al. [20] is 7.84 ± 0.18 kcal mol⁻¹ and 8.21 ± 0.18 kcal mol⁻¹ using W4 energies at the CCSD(T)/cc-pVQZ and experimental geometries, respectively. The most recent value of the $\Delta H_{f,298}^\circ$ of FOOF is 6.4 ± 0.7 kcal mol⁻¹ and was calculated using a coupled cluster-base composite approach [15]. These are only a few examples of this large deviation from experiment.

Predicting the conformational structure of FOOO has also been challenging. Freceer et al. [38] investigated the FOOO that formed by F + O₃ reaction and found that FO(O)₂ is the most stable structure with F-O being a weak bond (3.671 Å). However, FOOO was observed later as a stabilized intermediate in dilute mixtures of F₂ and O₃ in solid argon by FT-IR spectroscopy [39]. Based on the reported frequencies of FOOO, it is characterized as a FO-O₂ complex, and it cannot be a weak van der Waals complex [39], which differs from Freceer's stable structure [38], mentioned above. Quantum chemical studies by Li et al. [40] and Peiró-García et al. [41] of the F + O₃ reaction mechanisms using MP2/6-31G(d) and QCISD/6-311+G(d,p), respectively, also could not predict the FOOO ground state complex observed experimentally in the argon matrix [39]. A geometry optimization and frequency calculations of FOOO were performed by Roohi et al. [25] at the CCSD/aug-cc-pVDZ, CCSD/6-311+G(d), and QCISD/aug-cc-pVDZ levels of theory. Roohi's study [25] showed that the planar FOOO with dihedral angle of 0.0° is the most stable structure, with its calculated frequencies agreeing well with the reported experimental frequencies [39]. No $\Delta H_{f,298}^\circ$ for FOOO has been previously reported, to our knowledge. The structure of the corresponding hydride FOOOH has only been studied previously by MINDO [42] and by MP2/6-31G(d) [43]. As MP2 theory has encountered difficulty for calculating the FO and the OO bond lengths, an additional investigation of the FOOOH structure has to be done.

While methods such as CCSDT and QCISD are computationally demanding, *ab initio* composite methods have been developed to circumvent the computational demands of such methods. One such approach, the correlation consistent Composite Approach (ccCA) [44–46], is a method that has been demonstrated to be practical and reliable for the prediction of thermochemical properties, such as enthalpies of formation, ionization potentials, and electron affinities. The targeted accuracy of ccCA for main group molecules is to yield a mean absolute deviation of approximate chemical accuracy, 1 kcal mol⁻¹ at reduced computational cost. This is in contrast to coupled cluster-based composite methods, which generally strive for a chemical accuracy of ± 0.24 kcal mol⁻¹, such as the W4 composite method and the approach used by Feller *et al.* [15]. Because the performance of ccCA for a variety of halogen oxides and their related hydrides has not been examined in detail, it is of our interest to consider the utility of ccCA in describing oxygen fluorides, such as FOO, FOOF, and FOOO.

Density functionals provide another option, as, overall, functionals have a lower formal computational scaling than post-HF methods such as CCSD(T) and CCSDT, though DFT predictions such as for enthalpies of formation, in general, do not reach the accuracies achievable by composite methods, such as ccCA. Thus, they are system dependent methods and are worth considering for each system. For example, the Minnesota density functionals M06 [47] and M06-2X [47] were used by Meyer and Kass, [48] in conjunction with the correlation consistent basis sets [49–51] to assess their performance for predicting the $\Delta H_{f, 298}^\circ$'s of a set of chlorine oxides and related hydrides (ClO_x and ClO_xH , where $x = 1-4$) with respect to the $\Delta H_{f, 298}^\circ$'s of W4 method [34]. The capability of G3 [52] and G3B3 [53] for calculating $\Delta H_{f, 298}^\circ$'s of chlorine oxides were also investigated in the same study [48]. The main findings from the Meyer and Kass study are that M06 $\Delta H_{f, 298}^\circ$'s were found to differ by an average of $1.3 \text{ kcal mol}^{-1}$ from the W4 $\Delta H_{f, 298}^\circ$'s, while M06-2X resulted in larger error ($6.2 \text{ kcal mol}^{-1}$). G3 and G3B3 $\Delta H_{f, 298}^\circ$'s yielded an average error of $4.6 \text{ kcal mol}^{-1}$ and $6.5 \text{ kcal mol}^{-1}$, respectively. The author attributed the large errors of G3 and G3B3 $\Delta H_{f, 298}^\circ$'s to their poor predicted geometries. Although M06 and M06-2X functionals were examined for the prediction of the $\Delta H_{f, 298}^\circ$'s of chlorine oxides, the capability of M06 and M06-2X to predict structures and $\Delta H_{f, 298}^\circ$'s has not been assessed for other halogen oxides. Thus, it is of interest to evaluate these functionals for oxygen fluoride species, as well as examine the performance of G3 and G3B3 methods for these systems. G3 and G3B3 are used here, largely, as they were included in the Mayer and Kass study [48]. Though G4 is a more modern method, beginning with an MP4 reference energy is a costly start, and as shown in previous studies, G4 predicts very similar energies as G3 [54,55].

In the present study, the reliability of ccCA, G3, and G3B3 for the prediction of the $\Delta H_{f, 298}^\circ$'s of oxygen fluoride species was evaluated. In addition to these composite methods, the performance of M06 and M06-2X was also examined for predicting the structures and enthalpies of formation of oxygen fluoride species. A set of various oxygen fluorides were considered in this study, including FO, FOO, FOOO, and the related hydrides (FOH, FOOH, and FOOOH) and difluorides (FOF, FOOF, and FOOOF), where the $\Delta H_{f, 298}^\circ$'s of FOOO and FOOOH have not been reported previously. The effects of basis set size and spin contamination were also considered. For comparison, the $\Delta H_{f, 298}^\circ$'s of chlorine oxides and related hydrides have been provided, whereas full theoretical investigations for chlorine oxides and related hydrides can be found in the Meyer and Kass study and references therein [48].

2. COMPUTATIONAL METHODOLOGY

All calculations were performed using the Gaussian 09 software package [56]. The hybrid-meta-generalized gradient approximation (HMGGGA) Minnesota functionals (M06 [47] and M06-2X [47]) in conjunction with the augmented correlation consistent polarized valence basis sets (aug-cc-pVnZ), where $n = \text{D, T, Q}$, [49–51] were used to optimize the structures of all molecules under investigation. The tight- d correlation consistent basis set of Dunning et al., [57] aug-cc-pV($n+d$)Z, where $n = \text{D, T, Q}$, were used for chlorine. Frequency calculations were performed using M06 and M06-2X with each of the three basis sets to ensure that the structure is a stationary point. The enthalpies of formation for these structures were determined at the same level of theory. ccCA, G3, and G3B3, were also applied to predict the enthalpies of formation. In ccCA, geometry optimization and vibrational frequencies calculations are performed using B3LYP/aug-cc-pVTZ [44]. The harmonic vibrational frequencies are then corrected using a scale

factor of 0.989 as recommended in Ref. 44. The remaining steps in ccCA involve a series of single point energy calculations performed using the B3LYP/aug-cc-pVTZ geometry [44]. Several variants of ccCA can be used, which vary by the means used to extrapolate the MP2 energy (MP2/aug-cc-pV ∞ Z) to the CBS limit [44]. ccCA-S3 and ccCA-S4 utilize Schwartz’s inverse cubic and quartic extrapolation scheme, respectively [58]. ccCA-P utilizes Peterson’s mixed Gaussian/exponential extrapolation scheme [59] and ccCA-PS3 is an average of ccCA-P and ccCA-S3. In ccCA, several additive terms are combined with the MP2/CBS reference energy (extrapolated energy) including terms recovering the correlation energy beyond MP2, the core-valence and core-core correlation energies, and scalar-relativistic effects. All of these components are then added together, along with the zero point energy (ZPE) and an atomic spin-orbit correction, to provide the final ccCA energy. G3 [52] and G3B3 [53] both are composite methods that involve the same series of single point energy calculations though based upon different geometries. The geometry optimization in G3 is at the MP2(FULL)/6-31G(d) level of theory, while G3B3 uses the B3LYP/6-31G(d) level of theory. For open-shell systems (radicals) such as FOO and FOOO, which show a degree of spin contamination, RO-ccCA [60] and G3-RAD [61] energies were obtained and used to calculate their $\Delta H_{f,298}^\circ$ ’s. Gaussian 09 was used to determine these energies. The mean absolute deviations (MADs) of the calculated $\Delta H_{f,298}^\circ$ ’s were determined for all of the utilized methods with respect to the experimental values, unless otherwise noted.

3. RESULTS AND DISCUSSION

3.1 Structures

The structural parameters obtained by M06 and M06-2X for all of the species are listed in Table 1. The optimized structures at the B3LYP/aug-cc-pVTZ, MP2(full)/6-31G(d), and B3LYP/6-31G(d) levels, which are used for geometry optimizations in ccCA, G3, and G3B3, respectively, were also considered (shown in Table 1). Experimental structural parameters of FO [22], FOO [31], FOF [12], FOOF [11], and FOH [17], have been reported and were utilized as reference data to determine the performance of the considered methods. To the authors’ knowledge no experimental observations have been reported for the geometric parameters of FOOH, FOOO, and FOOOF. Thus, for these molecules theoretical results from rigorous methods such as coupled cluster are presented to calibrate the considered methods (CCSD(T)/TZ2P structure for FOOH [21], CCSD/6-311+G(d) structure for FOOO [25], and CCSD(T)/cc-pVTZ for FOOOF [19]).

The F-O bond length calculated by M06 and M06-2X for all set of molecules showed a systematic decrease in length when using the correlation consistent basis set family going from aug-cc-pVDZ, aug-cc-pVTZ, to aug-cc-pVQZ (Table 1). However, this decrease in the bond length while increasing basis set size does not occur for the O-O bond length as shown in Table 1, and can be dependent on the density functional being utilized. Both M06 and M06-2X underestimated the F-O and O-O bond lengths with respect to the corresponding experimental values. M06-2X predicted shorter F-O bond lengths and longer FO-O bond lengths than M06. The average difference between the aug-cc-pVTZ F-O bond lengths and the aug-cc-pVQZ F-O bond lengths is 0.005 Å for M06 and it is 0.002 Å for M06-2X, and for the FO-O bond length it is 0.003 Å for both functionals whereas the aug-cc-pVDZ bond lengths are generally longer. Yet, the M06/aug-cc-pVDZ and M06-2X/aug-cc-pVDZ predicted the closest geometries to the

reference data with average errors in the F-O bond length of 0.032 Å and 0.062 Å, respectively. Thus, increasing the basis set size will not always give the better structures for the systems under investigation. For open-shell species, such as FO, FOO, and FOOO, the degree of spin contamination resulting from the mixing of higher spin states into the wavefunction was calculated, as high spin contamination results in incorrect geometries and energies. Previous studies showed a high degree of spin contamination when studying FOO using other methods, such as MP2 [16,26]. No spin contamination was found when calculating FO, but it was present when calculating FOO and FOOO. The expectation values of the total spin, $\langle S^2 \rangle$, are listed in Table 2, where the optimal value for these radicals is $\langle S^2 \rangle = 0.75$. The effect of spin contamination becomes appreciable as the deviation of $\langle S^2 \rangle$ from 0.75 increases, and this deviation decreases with increasing the size of the basis sets, as shown in Table 2. Both UM06 and UM06-2X suffer from spin contamination associated with FOO (small) and FOOO (severe), as shown in Table 2. This error was corrected by using the restricted open-shell density functionals as shown in Table 1. ROM06 and ROM06-2X provided better structural parameters with respect to the reference data for FOO and FOOO than what UM06 and UM06-2X predicted. Thus, the ROM06 and ROM06-2X geometries were used later to calculate the enthalpies of formation. FOOOF was found to exist in two conformers. Both have very similar geometries but differ in the dihedral angles. One conformer has $d(\text{OOOF}) = 91.3^\circ$ and the other one has $d(\text{OOOF}) = 82.0^\circ$ [19]. Because the energy difference between the two conformers at the CCSD(T)/cc-pVTZ level is very small, 0.24 kcal mol⁻¹, with the $d(\text{OOOF}) = 82.0^\circ$ conformer having the lowest energy [19], only one conformer was included in the molecule test set. M06-2X described the structure of FOOOF better than M06 when compared to the CCSD(T) structure. Overall the geometries predicted by M06 are in better agreement with the reference data than M06-2X, although both functionals generally underestimated the F-O and the O-O bond lengths. Thus, for this set of molecules, doubling the amount of Hartree-Fock exchange from M06 to M06-2X does not improve the results.

As shown in Table 1, the F-O bond lengths obtained by B3LYP/aug-cc-pVTZ are in very good agreement (MAD of 0.01 Å) with respect to the reference data, with the exception of the F-O bond distance(s) in FOO and FOOF. The difference in F-O bond lengths is more than 0.01 Å (0.018 Å in FOO and 0.049 Å in FOOF) compared to experimental values. Although B3LYP/aug-cc-pVTZ did not predict very accurate bond lengths for FOO and FOOF, it provided a qualitatively correct description of the structures of these two molecules. The capability of B3LYP to describe the geometries has been noticed previously for some of the oxygen fluorides [26,35]. Quite similarly, the calculated F-O bond lengths at the B3LYP/6-31G(d) level were in very good agreement with respect to the reference data; however, not only is the F-O bond length underestimated in FOO and in FOOF (by 0.065 Å in FOO and 0.075 Å in FOOF), but also the F-O bond distance in FOOH was underestimated by about 0.016 Å using B3LYP/6-31G(d) in comparison to the reference data. Additionally, when using the 6-31G(d) basis set, the average error for B3LYP increased from 0.01 Å (obtained when using an aug-cc-pVTZ basis set) to 0.02 Å. Thus, again B3LYP with the small basis set 6-31G(d) is not enough to describe peroxide systems, such as FOO, FOOF, and FOOH. B3LYP in conjunction with aug-cc-pVTZ also resulted in the least average error of 0.01 Å (from the reference data) for the O-O bond length - compared to other methods. The effect of spin contamination for open shell systems using UB3LYP has been tested and the total spin operators $\langle S^2 \rangle$ are presented in Table 2, for each level of theory. The $\langle S^2 \rangle$ values for FOO show that the use of UB3LYP at either basis set levels

does not result in spin contamination, whereas for FOOO, both UB3LYP/aug-cc-pVTZ and UB3LYP/6-31G(d) levels resulted in large deviation from the optimal value $\langle S^2 \rangle = 0.75$. Consequently, the ROB3LYP is used to predict the geometry for FOOO, which is in agreement with the structure predicted by CCSD [25], as shown in Table 1. For FOOOF, B3LYP was able to predict the two conformers with $d(\text{OOOF}) = 91.3^\circ$ and with $d(\text{OOOF}) = 82.0^\circ$ and the B3LYP F-O and O-O bond lengths agree well with the CCSD(T) bond lengths.

The predicted geometries for FOF, FOH, and FOOH by MP2(full)/6-31g(d) agree well with the reference data within a 0.01 Å difference. However, MP2(full)/6-31g(d) predicted a 0.1 Å shorter F-O bond and a 0.1 Å longer O-O bond for FOOF compared to experimental bond lengths, this large difference in the bond lengths was also found previously using MP2/6-31g** [43]. Likewise, the F-O and O-O bond lengths predicted by MP2(full)/6-31g(d) for FOOOF are 0.08 Å and 0.05 Å shorter than CCSD(T) results, indicating that this level of theory is not enough to describe the peroxide's geometry. For the open-shell systems FOO and FOOO, the UMP2 method could not provide converged geometries due to large spin contamination.

As mentioned earlier for FOOOH, no reliable theoretical or experimental geometries have been reported. Based on the success of B3LYP/aug-cc-pVTZ method in predicting the FOOOF geometry compared to the CCSD(T)/cc-pVTZ, the B3LYP/aug-cc-pVTZ geometry for FOOOH is considered as the most reliable structure. For this compound, only one conformer $d(\text{FOOO}) = -87.4^\circ$ is found to be a stable structure. The B3LYP/6-31G(d) structure of FOOOH is quite similar to the structure at the B3LYP/aug-cc-pVTZ level, with a large difference of 0.03 Å in the FO-O bond length. M06 and M06-2X generally underestimated the bond lengths of FOOOH as compared to the B3LYP/aug-cc-pVTZ geometries. MP2 (full)/6-31g(d) predicted shorter F-O bond length and longer FO-O bond length than the B3LYP/aug-cc-pVTZ.

As a result of the above discussion, M06 and M06-2X are not recommended methods for predicting the geometries of oxygen fluorides and related hydrides and difluorides. MP2 performed well for most of the closed-shell compounds with the exception of the peroxides. The geometries obtained by B3LYP/aug-cc-pVTZ, shown in Figure 1, result in the lowest deviation from the reference data among the considered methods. As shown in Figure 1, using B3LYP/aug-cc-pVTZ supports conclusions from previous studies [12,17,31] that FOO, FOF, and FOH are bent with bond angles of 111.2° , 103.9° , and 98.6° , respectively. Different bond angles indicate that the bond angle opens more as the repulsion between bonds increases. Similarly, FOOF and FOOH have dihedral angles of 88.2° and 85.0° , respectively, in order to minimize the repulsion between bonds. FOOOF and FOOOH display a zigzag shape with $d(\text{FOOO}) = 93.6^\circ$, and $d(\text{FOOO}) = -87.4^\circ$, respectively. In contrast to all the peroxide systems, the stable conformer of FOOO is when $d(\text{FOOO}) = 0.0^\circ$. Intermolecular dispersion forces might be the cause of the stable FOOO structure.

3.2 Enthalpies of Formation ($\Delta H_{f, 298}^\circ$)

To provide a comparison between the performance of the utilized methods on chlorine oxide and oxygen fluoride species, the $\Delta H_{f, 298}^\circ$'s of chlorine oxides and related hydrides were determined using M06/aug-cc-pVQZ, M06-2X/aug-cc-pVQZ, ccCA-S3, G3, and G3B3 and are listed in Table 3. The MADs of the considered methods with respect to experiment for predicting $\Delta H_{f, 298}^\circ$'s are provided in Table 3 as well. These MADs are 1.1 (ccCA-S3), 2.1 (M06), 2.5 (M06-2X), 2.3 (G3), and 3.5 (G3B3) kcal mol⁻¹. The MAD of ccCA-S3 indicates that ccCA is a

reliable method in predicting energetics for chlorine oxides. M06 resulted in a MAD of 2.1 kcal mol⁻¹ for the calculated $\Delta H_{f, 298}^\circ$'s of chlorine oxides, which is 0.9 kcal mol⁻¹ greater than the MAD (1.2 kcal mol⁻¹) that resulted from the calculations done by Meyer and Kass [48]. This small difference arises from the use of a temperature correction approach that reduces the energy contributed from the low vibrational frequency modes as pointed out in Meyer and Kass study [47, 60]. In the present study, however, scale factors of 0.9853 (M06) and 0.9733 (M06-2X) [69] were used for the correction of the anharmonic vibrational frequencies in the computations. The $\Delta H_{f, 298}^\circ$'s calculated by M06 for chlorine oxides in the present study are in good agreement with the experimental values with the exception of ClO₃, which is known to be problematic for not only computational methods but also for experiments, as demonstrated by the error bar associated with the experimental $\Delta H_{f, 298}^\circ$ (± 3 kcal mol⁻¹) [70–72], as compared with smaller uncertainties for many main group species. Only ccCA-S3 and G3 predict the $\Delta H_{f, 298}^\circ$ of ClO₃ within the experimental uncertainty. The $\Delta H_{f, 298}^\circ$'s obtained by G3 are in relatively good agreement with the experiments (MAD = 2.3 kcal mol⁻¹), yet the ClO₂ $\Delta H_{f, 298}^\circ$ predicted by G3 overestimated the experimental value by ~4 kcal mol⁻¹. Similar to G3, M06-2X achieved a MAD of 2.5 kcal mol⁻¹, while the MAD for G3B3 was larger (MAD of 3.2 kcal mol⁻¹). Therefore, ccCA results in the lowest MAD from experiment for the prediction of energetic properties of chlorine oxides, followed by M06.

The $\Delta H_{f, 298}^\circ$'s for all of the oxygen fluoride species included in this study were calculated using M06 and M06-2X in conjunction with aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ at 298 K using the atomization energy approach and the results are shown in Table 4. A systematic decrease in the $\Delta H_{f, 298}^\circ$ values as the size of the basis set increases is observed, since the basis set with larger zeta (ξ) level recovers more energy, as shown in Table 4. The differences between energies determined using M06/aug-cc-pVTZ $\Delta H_{f, 298}^\circ$'s and those determined using M06/aug-cc-pVQZ $\Delta H_{f, 298}^\circ$'s is 0.1 - 1.1 kcal mol⁻¹ with an average difference of 0.5 kcal mol⁻¹, whereas the differences between energies determined using M06-2X/aug-cc-pVTZ $\Delta H_{f, 298}^\circ$'s and those determined using M06-2X/aug-cc-pVQZ $\Delta H_{f, 298}^\circ$'s is 0.3 - 1.9 kcal mol⁻¹ with an average difference of 1.2 kcal mol⁻¹. To evaluate the reliability of the utilized methods in calculating $\Delta H_{f, 298}^\circ$'s, the following reference data was used: experimental $\Delta H_{f, 298}^\circ$ values for FO, FOO, FOF, FOOF and FOH; the CCSD(T)/ANO4 $\Delta H_{f, 298}^\circ$ value for FOOH; and the extrapolated CCSD(T)/aug-cc-pV(T,Q)Z $\Delta H_{f, 298}^\circ$ value for FOOOF. For FOOO and FOOOH neither experimental nor theoretical $\Delta H_{f, 298}^\circ$ values are available. The MADs of the calculated $\Delta H_{f, 298}^\circ$'s with respect to the reference data were computed and provided in Table 4. Because of the well-known challenges of FOOF [13,20,21,28], the MAD was also calculated without FOOF. For ccCA, the ccCA-S3 variant was selected as it results in the lowest MAD for the $\Delta H_{f, 298}^\circ$'s of oxygen fluoride species with respect to the reference data as shown in Table 5 as compared with the other ccCA variants.

The calculated $\Delta H_{f, 298}^\circ$'s of FO by ccCA, M06, M06-2X, G3, G3B3 are within the reported experimental uncertainty (± 2.4 kcal mol⁻¹), as shown in Table 6. The $\Delta H_{f, 298}^\circ$'s of FO calculated by G3 and G3B3 are the nearest to the reported experimental value, while the $\Delta H_{f, 298}^\circ$ calculated by M06 deviated the most by 2.0 kcal mol⁻¹, but is still within the experimental uncertainty. The FO $\Delta H_{f, 298}^\circ$'s predicted by ccCA is also in very good agreement with experiment. For FOH, the $\Delta H_{f, 298}^\circ$'s calculated by ccCA is found to be the closest to the reported experimental value, while G3 and G3B3 provide $\Delta H_{f, 298}^\circ$'s that are 1.6 and 1.9 kcal mol⁻¹,

respectively, less than the experimental uncertainty. M06 and M06-2X underestimate the $\Delta H_{f,298}^\circ$'s of FOH by 5.46 and 4.56 kcal mol⁻¹, respectively, with respect to the experimental value. The ccCA $\Delta H_{f,298}^\circ$ of FOF is within the experimental error bar. G3 and G3B3 predict $\Delta H_{f,298}^\circ$'s of 6.5 and 6.8 kcal mol⁻¹, which are greater than the experimental uncertainty by 0.1 and 0.4 kcal mol⁻¹, respectively. M06 predicts a $\Delta H_{f,298}^\circ$ of FOF that is 3.2 kcal mol⁻¹ outside of the experimental uncertainty, while the $\Delta H_{f,298}^\circ$ calculated by M06-2X is 2.3 kcal mol⁻¹ outside of the experimental uncertainty.

For FOO, RO-ccCA and G3B3 give $\Delta H_{f,298}^\circ$'s that are outside the experimental error by 0.9 and 0.4 kcal mol⁻¹, respectively. These results demonstrate the utility of ccCA and G3B3 in predicting the FOO $\Delta H_{f,298}^\circ$. G3-RAD, one of the G3 versions developed for open-shell systems, is used instead of G3 to calculate the $\Delta H_{f,298}^\circ$'s of the radicals FOO and FOOO. The G3-RAD $\Delta H_{f,298}^\circ$ of FOO is also in good agreement with experiment. The calculated $\Delta H_{f,298}^\circ$ for FOO using ROM06 is above experimental value by 2.9 kcal mol⁻¹, whereas the $\Delta H_{f,298}^\circ$ calculated by ROM06-2X is 10.6 kcal mol⁻¹ greater than experiment. This large deviation can be explained by the poor geometry obtained using these M06 and M06-2X.

For FOOH, the CCSD(T)/ANO4 $\Delta H_{f,298}^\circ$ which is -10.4 ± 1.0 kcal mol⁻¹ [21], is being used as a reference value for this molecule. G3 and G3B3 predict $\Delta H_{f,298}^\circ$'s of FOOH of -10.3 and -10.2 kcal mol⁻¹, respectively, which are in excellent agreement with the CCSD(T) value. Conversely, the ccCA $\Delta H_{f,298}^\circ$ value of FOOH is -11.7 kcal mol⁻¹, which is higher than the CCSD(T) value by 1.3 kcal mol⁻¹. Based on the fact that oxygen fluoride molecules are considered highly correlated molecules, accounting for the core correlation correction in the method is highly important. Thus, ccCA $\Delta H_{f,298}^\circ$'s can be more accurate than the CCSD(T) energies because ccCA energies includes core-valence and core-core correction terms, whereas the reported CCSD(T) results used the frozen-core approximation [21]. G3B3 includes the high level correction term (HLC) in the energy. The HLC is calculated based on empirical parameters and it is added to the G3 energy to reduce the error between theory and experiment. Without the HLC the G3B3 $\Delta H_{f,298}^\circ$ deviates by ~ 7.0 kcal mol⁻¹ from the CCSD(T) value. M06 and M06-2X both underestimate the $\Delta H_{f,298}^\circ$ of FOOH by 2.6 and 1.0 kcal mol⁻¹, respectively. For FOOF, the ccCA $\Delta H_{f,298}^\circ$ value lies 3.6 kcal mol⁻¹ outside the error bar of the value reported by NIST-JANAF [36,37]. G3 and G3B3 predict $\Delta H_{f,298}^\circ$'s that are greater than experimental error bar by 4.2 and 3.8 kcal mol⁻¹, respectively. M06 and M06-2X give $\Delta H_{f,298}^\circ$'s larger than experiment by 6.6 and 10.9 kcal mol⁻¹, respectively. Several previous high-level theoretical studies have pointed out the discrepancy between experimental and calculated $\Delta H_{f,298}^\circ$'s, and suggested that the experiment to be revisited [15,20,21,28]. For example, high level methods predicted $\Delta H_{f,298}^\circ$ of FOOF of 9.6 ± 0.9 kcal mol⁻¹ (iCAS-CI+Q) [15], 8.7 ± 2.0 kcal mol⁻¹ (CCSD(T)/ANO4) [21], 7.84 ± 0.18 kcal mol⁻¹ (W4) [20], and 7.3 kcal mol⁻¹ (B3PW91/aug-cc-pVQZ) [28]. In addition, from this work the ccCA value of the $\Delta H_{f,298}^\circ$ of FOOF is 8.7 kcal mol⁻¹. Thus, the $\Delta H_{f,298}^\circ$'s provided by theoretical approaches is between 7-9 kcal mol⁻¹, whereas the experimental value is 4.6 ± 0.5 kcal mol⁻¹. Because of this large and consistent discrepancy, the MAD of the $\Delta H_{f,298}^\circ$'s is calculated with and without FOOF.

RO-ccCA, G3-RAD, ROM06, and ROM06-2X were employed to calculate the $\Delta H_{f,298}^\circ$ for FOOO and the predicted $\Delta H_{f,298}^\circ$'s are listed in Table 6. Due to the lack of reference data for FOOO, the $\Delta H_{f,298}^\circ$ of ccCA for FOOO (31.0 kcal mol⁻¹) is considered the most accurate based

on the previous successes of ccCA in predicting energetic properties (MAD of 1.01 kcal mol⁻¹ using ccCA-PS3 for main group molecules (G03/05 test set)) [44]. G3-RAD also predicts a very close value to the ccCA value (30.1 kcal mol⁻¹). However, including empirical parameters makes G3-RAD a system-dependent method. Thus, the RO-ccCA value is recommended. The computed $\Delta H_{f, 298}^\circ$ for FOOO using ROM06 is 5.7 kcal mol⁻¹ greater than the RO-ccCA value. M06-2X predicts very high $\Delta H_{f, 298}^\circ$'s for FOOO compared to the other methods. For FOOOH, the calculated $\Delta H_{f, 298}^\circ$'s of ccCA is considered the reference data for the same reason previously mentioned. The $\Delta H_{f, 298}^\circ$ of ccCA for FOOOH (-1.6 kcal mol⁻¹) is chemically rational since formation of hydride is usually exothermic with fluoride lowering its stability. In addition, G3B3 predicts as exothermic $\Delta H_{f, 298}^\circ$ as ccCA, but greater by 1.3 kcal mol⁻¹. G3 and M06 and M06-2X overestimated the $\Delta H_{f, 298}^\circ$ of FOOOH by 1.8, 4.2, and 4.5 kcal mol⁻¹, respectively, with respect to the ccCA value. Finally, ccCA successfully predicts the $\Delta H_{f, 298}^\circ$ of FOOOF with only a 0.2 kcal mol⁻¹ deviation from the extrapolated CCSD(T)/aug-cc-pV(T,Q)/Z value calculated previously by Huang et al.,[19] where other methods such as G2 and G96PW91/D95(3df) predicted $\Delta H_{f, 298}^\circ$'s that are > 7.0 kcal mol⁻¹ higher than the CCSD(T) value [73]. Here G3B3 $\Delta H_{f, 298}^\circ$ is also in good agreement with the CCSD(T) value, with a deviation of only 0.7 kcal mol⁻¹ between the two, but G3 $\Delta H_{f, 298}^\circ$ differs by 1.2 kcal mol⁻¹. This difference between G3B3 and G3 results typically comes from geometry optimization, with MP2 found to be insufficient to describe the structure of dioxygen fluoride species. M06 and M06-2X again overestimated the enthalpy of formation of FOOOF by 4.3 kcal mol⁻¹ with respect to the CCSD(T) value.

The MADs of the calculated $\Delta H_{f, 298}^\circ$'s for all the utilized methods with respect to the reference data were computed and provided in Table 6. The MADs of M06 and M06-2X as shown in Table 6 are 4.0 and 5.2 kcal mol⁻¹ (3.5 and 4.3 kcal mol⁻¹ without FOOF), respectively. Thus, compared to the chlorine oxides in Table 3, M06 and M06-2X do not perform well for oxygen fluoride species. That can be attributed to the poor geometries obtained by M06 and M06-2X. Because of the deficiencies in the M06 and M06-2X computed geometries, single point M06 and M06-2X energy calculations were performed using the B3LYP/aug-cc-pVTZ geometries to examine the performances of M06 and M06-2X for oxygen fluorides energy calculations. $\Delta H_{f, 298}^\circ$ and MAD's were calculated and listed in Table 7. However, no improvement is noticed in the M06 and M06-2X $\Delta H_{f, 298}^\circ$'s when using B3LYP geometries. That supports our conclusion that M06 and M06-2X are not considered reliable methods to predict structures and energetic properties for oxygen fluorides. G3 and G3B3 (including the G3-RAD values) perform well with MAD's of 1.5 kcal mol⁻¹ for both methods (0.9 kcal mol⁻¹ for both methods without FOOF). This performance is not surprising taking into account the inclusion of the HLC term in the G3 and G3B3 energy. For example, the G3B3 $\Delta H_{f, 298}^\circ$ of FO without the HLC term is 30.3 kcal mol⁻¹, a value that is greater by 3.8 kcal mol⁻¹ than the G3B3 $\Delta H_{f, 298}^\circ$ listed in Table 6. The MAD of the G3 and G3B3 methods (1.5 kcal mol⁻¹) is much smaller for the oxygen fluorides than for the chlorine oxides (2.3 kcal mol⁻¹ for G3 and 3.5 kcal mol⁻¹ for G3B3), so G3 and G3B3 perform better for oxygen fluorides than for chlorine oxides. The MAD of ccCA-S3 is 1.4 kcal mol⁻¹ (0.9 kcal mol⁻¹ without FOOF) for oxygen fluorides and is 1.1 kcal mol⁻¹ for chlorine oxides. This indicates a capability of ccCA to predict reliable energetic properties for halogen oxides.

In addition, a comparison between the calculated $\Delta H_{f, 298}^\circ$'s in this study and the recent ATcT values of the $\Delta H_{f, 298}^\circ$'s [74,75] of FO, FOH, FOF, FOO, FOOF, and FOOOF are

examined. The ATcT tables use artificial intelligence algorithms to reduce the uncertainties in the experimentally measured $\Delta H_{f, 298}^\circ$'s by combining experimental and highly accurate theoretical thermochemical data [74,75]. As shown in Table 8, the uncertainties of the ATcT values of FO, FOH, FOF, and FOO decreased in comparison to the NIST-JANAF values (Table 6). Thus, to evaluate our methods against the ATcT values, the MADs of the calculated $\Delta H_{f, 298}^\circ$'s for all the utilized methods with respect to the ATcT values were computed and provided in Table 8. The MADs of ccCA-S3, M06, M06-2X, G3, and G3B3 were all lowered by 0.5-0.9 kcal mol⁻¹ in comparison with the MADs shown in Table 6 (with ccCA-S3 providing the lowest MAD, at 0.6 kcal mol⁻¹). The large difference in the MADs is likely attributed to the large difference between the ATcT $\Delta H_{f, 298}^\circ$ for FOOF (8.04±0.09 kcal mol⁻¹) and the NIST-JANAF value (4.6 ± 0.5 kcal mol⁻¹).

4. CONCLUSION

The capability of ccCA, G3, and G3B3 for the prediction of the enthalpies of formation of oxygen fluoride species was evaluated. In addition, the performance of M06 and M06-2X in conjunction with the correlation consistent basis sets (aug-cc-pVnZ), where $n = D, T, Q$, was also examined for predicting the structures and enthalpies of formation of oxygen fluoride species. An important finding from this study is that though M06 and M06-2X are useful functionals for many main group species (including chlorine oxides), M06 and M06-2X were less successful in the prediction of reasonable structures and $\Delta H_{f, 298}^\circ$'s for oxygen fluorides, oxygen difluorides, and related hydrides. This could be generalized to systems containing F-O and/or O-O bonds (e.g. peroxides and polyoxides). Geometries predicted by B3LYP/aug-cc-pVTZ are generally in good agreement with the listed reference data. When calculating the enthalpies of formation, ccCA-S3 provides the lowest MAD (1.4 kcal mol⁻¹ with respect to the reference data; 0.9 kcal mol⁻¹ excluding FOOF) without any parameterized energies. While ccCA-S3 provides the smallest MAD of the four different CBS extrapolation formulas considered for this set of molecules, other ccCA variants, such as ccCA-PS3, have been found to be useful in previous studies [44,54]. G3 and G3B3 achieved a MAD that is greater than ccCA-S3 by only 0.1 kcal mol⁻¹ with respect to the reference data while incorporating an empirical parameter that is intended to reduce the overall MAD of G3 and G3B3 (or MAD of 0.9 kcal mol⁻¹ excluding FOOF, which is identical to ccCA-S3 in this case). The performance of G3 and G3B3 for chlorine oxides is not as good as for oxygen fluorides. ccCA-S3 predictions of the $\Delta H_{f, 298}^\circ$'s of both the oxygen fluorides and of the chloride oxides species are in good agreement with the experimental values. In addition, when comparing the calculated $\Delta H_{f, 298}^\circ$'s to the ATcT values, ccCA-S3 provides the lowest MAD (0.6 kcal mol⁻¹) in comparison to the other methods including in this study. The enthalpies of formation for FOOF and FOOFH are predicted to be 31.0 and -1.6 kcal mol⁻¹, respectively, by the ccCA-S3 method. Overall, the use of the correlation consistent Composite Approach (ccCA) is recommended for such systems, with promise for other halogen systems and peroxides.

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Figure 1. B3LYP/aug-cc-pVTZ structures of the oxygen fluorides species included in this study.

Table 1. Structural parameters of the oxygen fluoride species at different level of theories, bond lengths are in Angstroms and bond angles and dihedral angles are in degree.

FO			
Method/Basis set	r (FO)		
M06/aug-cc-pVDZ	1.332		
M06/aug-cc-pVTZ	1.328		
M06/aug-cc-pVQZ	1.324		
M062X/aug-cc-pVDZ	1.329		
M062X/aug-cc-pVTZ	1.329		
M062X/aug-cc-pVQZ	1.325		
B3LYP/aug-cc-pVTZ	1.351		
B3LYP/6-31g(d)	1.354		
MP2(full)/6-31g(d)	1.344		
Experiment ^a	1.354		
FOH			
Method/Basis set	r (FO)	r (OH)	a (FOH)
M06/aug-cc-pVDZ	1.408	0.973	99.1
M06/aug-cc-pVTZ	1.405	0.969	99.2
M06/aug-cc-pVQZ	1.401	0.966	99.3
M062X/aug-cc-pVDZ	1.401	0.971	99.3
M062X/aug-cc-pVTZ	1.400	0.968	99.4
M062X/aug-cc-pVQZ	1.397	0.967	99.5
B3LYP/aug-cc-pVTZ	1.430	0.971	98.6
B3LYP/6-31g(d)	1.434	0.977	97.8
MP2(full)/6-31g(d)	1.444	0.979	97.1
Experiment ^b	1.4350 ± 0.0031	0.9657 ± 0.0016	97.54 ± 0.50
FOF			
Method/Basis set	r (FO)	a (FOF)	
M06/aug-cc-pVDZ	1.380	103.5	
M06/aug-cc-pVTZ	1.377	103.6	
M06/aug-cc-pVQZ	1.374	103.7	
M062X/aug-cc-pVDZ	1.376	102.9	
M062X/aug-cc-pVTZ	1.374	103.0	
M062X/aug-cc-pVQZ	1.371	103.1	
B3LYP/aug-cc-pVTZ	1.403	103.9	
B3LYP/6-31g(d)	1.409	103.9	
MP2(full)/6-31g(d)	1.423	102.6	
Experiment ^c	1.412	103.1	
FOO			
Method/Basis set	r (FO)	r (OO)	a (FOO)
M06/aug-cc-pVDZ	1.811	1.177	110.7
M06/aug-cc-pVTZ	1.752	1.171	110.6
M06/aug-cc-pVQZ	1.747	1.170	110.7
ROM06/aug-cc-pVDZ	1.589	1.182	110.6
ROM06/aug-cc-pVTZ	1.580	1.178	110.6
ROM06/aug-cc-pVQZ	1.572	1.178	110.7
M062X/aug-cc-pVDZ	2.090	1.184	111.2

M062X/aug-cc-pVTZ	1.520	1.190	110.0
M062X/aug-cc-pVQZ	1.519	1.187	110.1
ROM062X/aug-cc-pVDZ	1.508	1.194	109.9
ROM062X/aug-cc-pVTZ	1.500	1.194	110.0
ROM062X/aug-cc-pVQZ	1.500	1.191	110.1
B3LYP/aug-cc-pVTZ	1.618	1.188	111.2
B3LYP/6-31g(d)	1.571	1.211	111.0
MP2(full)/6-31g(d)	-	-	-
Experiment ^d	1.649±0.013	1.200±0.013	111.2±0.36

FOOH

Method/Basis set	<i>r</i> (FO)	<i>r</i> (OO)	<i>r</i> (OH)	<i>a</i> (FOO)	<i>a</i> (OOH)	<i>d</i> (FOOH)
M06/aug-cc-pVDZ	1.447	1.343	0.977	105.9	104.0	85.5
M06/aug-cc-pVTZ	1.438	1.346	0.972	105.9	103.9	85.2
M06/aug-cc-pVQZ	1.434	1.343	0.970	106.0	104.0	85.4
M062X/aug-cc-pVDZ	1.419	1.358	0.973	105.3	103.6	84.6
M062X/aug-cc-pVTZ	1.415	1.361	0.970	105.4	103.6	84.6
M062X/aug-cc-pVQZ	1.412	1.357	0.968	105.5	103.7	84.7
B3LYP/aug-cc-pVTZ	1.470	1.365	0.974	106.3	103.7	85.0
B3LYP/6-31g(d)	1.465	1.376	0.981	106.1	102.9	83.1
MP2(full)/6-31g(d)	1.468	1.39	0.981	105.0	102.0	83.1
Experiment	-	-	-	-	-	-
CCSD(T)/TP2Z ^c	1.481	1.393	0.969	105.4	101.9	84.5

FOOF

Method/Basis set	<i>r</i> (FO)	<i>r</i> (OO)	<i>a</i> (FOO)	<i>d</i> (FOOF)
M06/aug-cc-pVDZ	1.506	1.217	108.6	87.2
M06/aug-cc-pVTZ	1.494	1.219	108.5	86.9
M06/aug-cc-pVQZ	1.485	1.221	108.6	87.0
M062X/aug-cc-pVDZ	1.426	1.285	106.6	85.9
M062X/aug-cc-pVTZ	1.420	1.289	106.7	85.7
M062X/aug-cc-pVQZ	1.419	1.286	106.8	85.8
B3LYP/aug-cc-pVTZ	1.523	1.227	109.3	88.1
B3LYP/6-31g(d)	1.497	1.266	108.3	86.7
MP2(full)/6-31g(d)	1.496	1.291	106.9	85.8
Experiment ^f	1.575±0.003	1.217±0.003	109.5±0.5	87±0.5

FOOO

Method/Basis set	<i>r</i> (FO)	<i>r</i> (FO-O), <i>r</i> (FOO-O)	<i>a</i> (FOO), <i>a</i> (OOO)	<i>d</i> (FOOO)
M06/aug-cc-pVDZ	1.338	2.469, 1.196	97.8, 110.8	0.0
M06/aug-cc-pVTZ	1.335	2.408, 1.191	93.0, 106.5	0.0
M06/aug-cc-pVQZ	1.331	2.449, 1.189	92.4, 105.9	0.0
ROM06/aug-cc-pVDZ	1.357	1.704, 1.192	100.2, 110.1	0.0
ROM06/aug-cc-pVTZ	1.354	1.687, 1.189	100.9, 110.5	0.0
ROM06/aug-cc-pVQZ	1.350	1.681, 1.188	101.1, 110.7	0.0
M062X/aug-cc-pVDZ	1.331	2.598, 1.191	88.5, 103.4	0.0
M062X/aug-cc-pVTZ	1.333	2.537, 1.187	90.4, 105.6	0.0
M062X/aug-cc-pVQZ	1.327	2.702, 1.187	91.0, 107.8	0.0
ROM062X/aug-cc-pVDZ	1.360	1.589, 1.204	103.3, 112.1	0.0
ROM062X/aug-cc-pVTZ	1.359	1.575, 1.205	103.9, 112.4	0.0
ROM062X/aug-cc-pVQZ	1.356	1.573, 1.203	104.0, 112.5	0.0
B3LYP/aug-cc-pVTZ	1.354	2.715, 1.204	101.1, 113.8	0.0

B3LYP/6-31g(d)	1.360	2.504, 1.211	91.0, 103.3	0.0
ROB3LYP/aug-cc-pVTZ	1.379	1.709, 1.201	101.2, 111.2	0.0
ROB3LYP/6-31g(d)	1.380	1.710, 1.214	100.3, 110.2	0.0
B97D/aug-cc-pVTZ	1.385	1.842, 1.204	100.9, 111.3	0.0
MP2(full)/6-31g(d)	-	-	-	-
Experiment	-	-	-	-
CCSD/6-311+G(d) ^g	1.378	1.745, 1.200	100.5, 111.5	0.0

FOOOH

Method/Basis set	r (FO)	r (FO-O), r (O-OH)	r (OH)	a (FOO), a (OOO), a (OOH)	d (FOOO)	d (OOOH)
M06/aug-cc-pVDZ	1.483	1.290, 1.427	0.974	106.5, 109.0, 101.1	-85.8	91.7
M06/aug-cc-pVTZ	1.471	1.292, 1.428	0.970	106.5, 109.0, 101.1	-85.7	91.4
M06/aug-cc-pVQZ	1.466	1.291, 1.424	0.968	106.6, 109.1, 101.2	-85.6	91.8
M062X/aug-cc-pVDZ	1.427	1.331, 1.406	0.972	105.3, 107.9, 101.8	-84.0	91.4
M062X/aug-cc-pVTZ	1.423	1.333, 1.407	0.967	105.5, 108.1, 102.1	-84.0	90.1
M062X/aug-cc-pVQZ	1.421	1.330, 1.403	0.968	105.6, 108.2, 102.2	-83.9	90.3
B3LYP/aug-cc-pVTZ	1.502	1.303, 1.461	0.972	107.3, 109.6, 100.7	-87.4	96.0
B3LYP/6-31g(d)	1.485	1.331, 1.454	0.979	106.3, 108.8, 99.9	-84.9	89.0
MP2(full)/6-31g(d)	1.481	1.358, 1.450	0.981	104.9, 107.5, 99.7	-83.2	87.0
Experiment	-	-	-	-	-	-

FOOOF

Method/Basis set	r (FO)	r (OO)	a (FOO), a (OOO)	d (FOOO)
M06/aug-cc-pVDZ	1.419	1.355	106.2, 109.0	± 93.0
M06/aug-cc-pVTZ	1.413	1.355	106.2, 109.1	± 92.5
M06/aug-cc-pVQZ	1.410	1.353	106.3, 109.2	± 92.4
M062X/aug-cc-pVDZ	1.403	1.360	105.3, 108.1	± 90.9
M062X/aug-cc-pVTZ	1.400	1.360	105.7, 108.3	± 90.8
M062X/aug-cc-pVQZ	1.399	1.357	105.7, 108.5	± 91.0
B3LYP/aug-cc-pVTZ	1.440	1.377	106.6, 109.3	± 93.6
B3LYP/6-31g(d)	1.440	1.386	105.8, 108.7	± 90.5
MP2(full)/6-31g(d)	1.365	1.340	105.6, 108.2	± 90.1
Experiment	-	-	-	-
CCSD(T)/cc-pVTZ ^h	1.444	1.385	105.5, 108.3	± 91.3

^a Ref. [22]. ^b Ref. [17]. ^c Ref. [12]. ^d Ref. [31]. ^e CCSD(T)/TZ2P: Ref. [21]. ^f Ref. [11]. ^g CCSD/6-311+G(d): Ref. [25]. ^h CCSD(T)/cc-pVTZ: Ref. [19].

Table 2. The expectation value of the total spin $\langle S^2 \rangle$.

Molecule	Method/Basis set	$\langle S^2 \rangle$
FOO	M06/aug-cc-pVDZ	0.756
	M06/aug-cc-pVTZ	0.754
	M06/aug-cc-pVQZ	0.754
	M062X/aug-cc-pVDZ	0.782
	M062X/aug-cc-pVTZ	0.750
	M062X/aug-cc-pVQZ	0.750
	B3LYP/aug-cc-pVTZ	0.750
	B3LYP/6-31g(d)	0.7509
FOOO	M06/aug-cc-pVDZ	0.892
	M06/aug-cc-pVTZ	0.782
	M06/aug-cc-pVQZ	0.782
	M062X/aug-cc-pVDZ	0.803
	M062X/aug-cc-pVTZ	0.780
	M062X/aug-cc-pVQZ	0.807
	B3LYP/aug-cc-pVTZ	0.790
	B3LYP/6-31g(d)	0.776

Table 3. Enthalpies of formation for chlorine oxides and related hydrides.

Compd.	$\Delta H^\circ_{f, 298\text{ K}} (\text{kcal mol}^{-1})$					
	ccCA-S3	M06 ^a	M06-2X ^a	G3	G3B3	Expt.
ClO	25.3	23.1	23.5	25.9	26.7	24.29 ± 0.03^b
ClO₂	23.9	21.2	26.8	26.8	27.6	$22.6 \pm 0.3^{b,c}$
ClO₃	44.0	40.5	50.2	48.3	51.0	46 ± 3^d
ClO₄	57.7	52.6	65.4	66.0	65.5	-
HOCl	-19.5	-18.0	-19.3	-17.4	-16.9	-18.4 ± 0.03^e
HOClO	3.5	4.6	6.5	6.4	7.3	-
HOClO₂	-2.8	-3.9	3.3	2.0	3.8	-
HOClO₃	-0.8	-3.4	5.5	5.6	8.7	-
MAD	1.1	2.1	2.5	2.3	3.5	-

^a M06 and M06-2X in conjunction with aug-cc-pV(Q+d)Z for chlorine and aug-cc-pVQZ for oxygen and hydrogen.

^b Ref. [76]. ^c Ref. [77]. ^d Ref. [70–72] ^e Ref. [78].

Table 4. Enthalpies of formation for the oxygen fluoride species using M06 and M06-2X paired with the correlation consistent basis sets.

Compd.	$\Delta H_{f, 298\text{ K}}^{\circ}$ (kcal mol ⁻¹)						Reference data ^a
	M06			M06-2X			
	aDZ	aTZ	aQZ	aDZ	aTZ	aQZ	
FO	29.6	28.5	28.1	29.1	28.3	27.5	26.1±2.4
FOH	-16.9	-17.3	-17.7	-16.4	-18.3	-18.6	-23.16±1.2
FOF	12.9	9.7	9.6	11.5	9.6	8.7	5.9±0.5
FOO	10.6	9.5	9.0	18.3	16.0	14.5	6.1±0.5
FOOH	-6.0	-6.9	-7.6	-5.6	-7.6	-8.4	-10.4±1.0 ^b
FOOF	14.1	11.3	11.2	18.6	16.9	15.5	4.6±0.5
FOOO	40.3	37.8	36.7	43.4	43.2	41.3	-
FOOOH	4.9	3.5	2.6	6.2	4.1	2.9	-
FOOOF	35.3	31.5	30.9	34.4	32.7	30.9	26.6 ^c
MAD	6.3	4.4	4.0	7.7	6.0	5.2	
MAD w/o FOOF	5.7	4.0	3.5	6.7	5.0	4.3	

aDZ: aug-cc-pVDZ

aTZ: aug-cc-pVTZ

aQZ: aug-cc-pVQZ

^a NIST-JANAF Tables: Ref. [36,37].

^b CCSD(T)/ANO4: Ref. [21].

^c Extrapolated CCSD(T)/aug-cc-pV(T,Q)Z: Ref. [19].

Table 5. Enthalpies of formation for the oxygen fluoride species using the four different variant of ccCA method.

Compd.	$\Delta H_{f, 298 \text{ K}}^{\circ} \text{ (kcal mol}^{-1}\text{)}$				Reference data ^a
	ccCA-P	ccCA-S3	ccCA-PS3	ccCA-S4	
FO	27.3	27.0	27.2	27.3	26.1±2.4
FOH	-21.1	-21.6	-21.4	-21.1	-23.16±1.2
FOF	6.6	6.2	6.4	6.7	5.9±0.5
FOO	8.1	7.5	7.8	8.1	6.1±0.5
FOOH	-11.0	-11.7	-11.3	-10.9	-10.4±1.0 ^b
FOOF	9.4	8.7	9.0	9.4	4.6±0.5
FOOO	31.8	31.0	31.4	31.8	-
FOOOH	-0.7	-1.6	-1.1	-0.6	-
FOOOF	27.8	26.8	27.3	27.8	26.6 ^c
MAD	1.8	1.4	1.6	1.8	-
MAD w/o FOOF	1.3	0.9	1.1	1.3	-

^a NIST-JANAF Tables: Ref. [36,37].

^b CCSD(T)/ANO4: Ref. [21].

^c Extrapolated CCSD(T)/aug-cc-pV(T,Q)Z: Ref. [19].

Table 6. Calculated enthalpies of formation for the oxygen fluoride species using all methods and the MADs of these methods with respect to the reference data.

Compd.	$\Delta H^\circ_{f, 298 \text{ K}} \text{ (kcal mol}^{-1}\text{)}$					Reference data ^b
	ccCA-S3	M06 ^a	M06-2X ^a	G3	G3B3	
FO	27.0	28.1	27.5	26.1	26.5	26.1±2.4
FOH	-21.6	-17.7	-18.6	-20.4	-20.1	-23.16±1.2
FOF	6.2	9.6	8.7	6.5	6.8	5.9±0.5
FOO	7.5 ^e	9.0 ^f	14.5 ^f	7.1 ^g	7.0	6.1±0.5
FOOH	-11.7	-7.6	-8.4	-10.3	-10.2	-10.4±1.0 ^c
FOOF	8.7	11.2	15.5	9.3	8.9	4.6±0.5
FOOO	31.0 ^e	36.7 ^f	41.3 ^f	30.1 ^g	30.1 ^g	-
FOOOH	-1.6	2.6	2.9	0.2	-0.3	-
FOOOF	26.8	30.9	30.9	27.8	27.3	26.6 ^d
MAD	1.4	4.0	5.2	1.5	1.5	-
MAD w/o FOOF	0.9	3.5	4.3	0.9	0.9	-

^a M06 and M06-2X in conjunction with aug-cc-pVQZ.

^b NIST-JANAF Tables: Ref. [36,37].

^c CCSD(T)/ANO4: Ref. [21].

^d Extrapolated CCSD(T)/aug-cc-pV(T,Q)Z: Ref. [19].

^e Using RO-ccCA.

^f Using ROM06 and ROM06-2X.

^g Using G3-RAD.

Table 7. Calculated enthalpies of formation for the oxygen fluoride species using M06 and M06-2X methods based on B3LYP/aug-cc-pVTZ geometries.

Compd.	$\Delta H^\circ_{f, 298 \text{ K}} \text{ (kcal mol}^{-1}\text{)}$		
	B3LYP ^a //M06 ^b	B3LYP ^a //M06-2X ^b	Reference data ^c
FO	28.4	27.7	26.1±2.4
FOH	-17.5	-18.5	-23.16±1.2
FOF	10.2	9.3	5.9±0.5
FOO	9.3	15.0	6.1±0.5
FOOH	-6.9	-7.7	-10.4±1.0 ^d
FOOF	11.8	19.9	4.6±0.5
FOOO	34.7	47.5	-
FOOOH	4.9	4.5	-
FOOOF	31.8	32.1	26.6 ^e
MAD	4.5	6.0	-
MAD w/o FOOF	4.0	4.4	-

^a B3LYP/aug-cc-pVTZ.

^b M06/aug-cc-pVQZ and M06-2X/aug-cc-pVQZ

^c NIST-JANAF Tables: Ref. [36,37].

^d CCSD(T)/ANO4: Ref. [21].

^e Extrapolated CCSD(T)/aug-cc-pV(T,Q)Z: Ref. [19].

Table 8. Calculated Enthalpies of formation for the oxygen fluoride species using all methods and the MADs of these methods with respect to the ATcT values.

Compd.	$\Delta H_{f, 298 \text{ K}}^{\circ} \text{ (kcal mol}^{-1}\text{)}$					ATcT ^b
	ccCA-S3	M06 ^a	M06-2X ^a	G3	G3B3	
FO	27.0	28.1	27.5	26.1	26.5	26.51±0.04
FOH	-21.6	-17.7	-18.6	-20.4	-20.1	-20.85±0.05
FOF	6.2	9.6	8.7	6.5	6.8	5.91±0.06
FOO	7.5 ^e	9.0 ^f	14.5 ^f	7.1 ^g	7.0	5.99±0.06
FOOH	-11.7	-7.6	-8.4	-10.3	-10.2	-
FOOF	8.7	11.2	15.5	9.3	8.9	8.04±0.09
FOOO	31.0 ^c	36.7 ^d	41.3 ^d	30.1 ^e	30.1 ^e	-
FOOOH	-1.6	2.6	2.9	0.2	-0.3	-
FOOOF	26.8	30.9	30.9	27.8	27.3	26.63±1.86
MAD	0.6	3.1	4.7	0.8	0.7	

^a M06 and M06-2X in conjunction with aug-cc-pVQZ.

^b ATcT: Ref. [74,75].

^c Using RO-ccCA.

^d Using ROM06 and ROM06-2X.

^e Using G3-RAD.

Graphical abstract

MADs of the enthalpies of formation of oxygen fluoride species (excluding FOOF).