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Density Functional Study of Structures and Electron Affinities of $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$

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Abstract: The structures, electron affinities and bond dissociation energies of $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ species have been investigated with five density functional theory (DFT) methods with DZP++ basis sets. The planar $\text{F-Br}\dots\text{O}_2\dots\text{O}_2$ complexes possess $^3\text{A}'$ electronic state for neutral molecule and $^4\text{A}'$ state for the corresponding anion. Three types of the neutral-anion energy separations are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The EA_{ad} value predicted by B3LYP method is 4.52 eV. The bond dissociation energies D_e ($\text{BrO}_4\text{F} \rightarrow \text{BrO}_{4-m}\text{F} + \text{O}_m$) ($m = 1-4$) and D_e^- ($\text{BrO}_4\text{F}^- \rightarrow \text{BrO}_{4-m}\text{F}^- + \text{O}_m$ and $\text{BrO}_4\text{F}^- \rightarrow \text{BrO}_{4-m}\text{F} + \text{O}_m^-$) are predicted. The adiabatic electron affinities (EA_{ad}) were predicted to be 4.52 eV for $\text{F-Br}\dots\text{O}_2\dots\text{O}_2$ ($^3\text{A}' \leftarrow ^4\text{A}'$) (B3LYP method).

Keywords: density functional theory; bromine fluorine oxides; DFT-based descriptors; EA

1. Introduction

In recent days, density functional theory (DFT) has been enjoying tremendous success in electronic structure calculations for molecules and solids alike [1–8]. The DFT methods are able to describe the electronic structure of these systems with accuracies comparable to traditional correlated molecular

orbital methods at a decreased computational cost. Furthermore these techniques are observed to assign more bonding character to the Lewis system in which the nucleophilic reaction occurs [9]. The DFT-based global and local properties (namely, DFT descriptors), such as Fukui functions, global and local hardness or softness [10,11], have already been used for reliable predictions in various types of electrophilic and nucleophilic reactions on a diversity of material structures [1-9,12-16]. In some sense, the DFT-descriptors provide us with more rigorous alternatives than the classical frontier orbital analysis. Chatterjee's group have already used the DFT-descriptors for predictions in electrophilic and nucleophilic reactions in the case of zeolites and clay materials with or without solvent environment [1-7].

On the other hand, the bromine, chlorine, and fluorine oxides are known to be important in lower stratospheric ozone depletion, and have been the subjects of intense studies in recent years [17-26, and references cited therein]. Relevant bromine oxide fluorides, represent intriguing ternary molecules involving covalent bond between highly electronegative atoms, possessing a large number of unpaired electrons, resulting in strong lone pair-lone pair repulsions. Therefore, the hypervalent structures of these species could be characterized. As early as 1972, Johnson *et al.* [27] reported the thermodynamic properties of Br(VII) FBrO_3 species. In 1976, Appelman *et al.* [28] characterized the molecular structure of gaseous perbromyl fluoride (FBrO_3), and Gillespie and Spekkens [29] prepared and characterized potassium difluorodioxobromate (BrO_2F_2^-) and tetrafluoro-oxobromate (BrOF_4^-). In 1978, Christie *et al.* [30] reported the vibrational frequencies and assignment of BrOF_3 . In 2005, Lehmann *et al.* [31] reported synthesis and characterization of salts containing the bromine (VII) BrO_3F_2^- anion; last year, Lehmann *et al.* [32] also reported the characterization of BrO_3F and ClO_3F to $[\text{XO}_2][\text{SbF}_6]$ ($\text{X} = \text{Cl}, \text{Br}$) by single crystal X-ray diffraction, raman spectroscopy, and computational methods. The results showed that of a few computational methods, the DFT functional, B3LYP in combination with the aug-cc-pVTZ basis set, and the QCISD and CCSD(T) calculations provided the most reliable correlation with the experimental geometry and vibrational frequencies of BrO_2^+ [33] and likely provide reliable estimates of the geometric parameters and vibrational frequencies of BrO_3^+ , as well as benchmarks for calculations involving bromine fluoride and oxide fluoride species [33]. Correspondingly, the density functional theory (DFT) in conjunction with DZP++ basis set has also localized these Br-hypervalent ternary structures to be minimum on the potential energy surfaces (PES) [34,35]. The planar/linear $\text{FBrO}/\text{FBrO}^-$, pseudo-trigonal bipyramid $\text{F}(\text{F}_2)\text{Br}=\text{O}$ (C_s symmetric) [34] and $[\text{F}-(\text{BrO}_2)-\text{F}]^-$ (C_{2v}) anionic [29], and quasi-octahedral $(\text{OBr}-\text{F}_4)^-$ (C_{4v}) [34,29] Br(V) structures have been found to be the lowest-lying isomers. However, the hypervalent FBrO_2 , FBrO_3 [35], and their corresponding anionic isomers are local minima on the PES. These DFT methods, especially the hybrid DFT methods (BHLYP and B3LYP) are reliable to predict the bond lengths and bond angles [32]. Besides the rich fluoride chemistry of the III and V oxidation states of Br oxides, the fluoride ion transfer reactions containing Br(VII) are scarce and have only been established by the syntheses of the ternary bromine oxide fluorides, BrO_3F_2^- [31]. In this work, we report the systemic theoretical investigation of the similar $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ species, which may be of importance in atmospheric chemistry.

DFT/DZP++ scheme has been shown to be successful in prediction of electron affinities (EAs) of many species, such as $\text{BrOF}_n/\text{BrOF}_n^-$, $\text{FBrO}_2/\text{FBrO}_3$, $\text{Br}_2\text{O}_n/\text{Br}_2\text{O}_n^-$, $\text{BrClF}_n/\text{BrClF}_n^-$ and $\text{SF}_5\text{O}_n/\text{SF}_5\text{O}_n^-$ ($n = 1-3$) species [34-38]. These studies and others have demonstrated that the DFT/DZP++ methods

can predict electron affinities (EAs) in a good accuracy [39]. In addition, these methods are reliable for the geometry optimization of the neutral radicals and their anion.

The aim of the present work is to apply five DFT methods to predict the electron affinities of ternary bromine oxide fluoride, BrO_4F , as well as the equilibrium geometries, harmonic vibrational frequencies, and bond dissociation energies. Four forms of the electron affinities are calculated, evaluated as the neutral–anion energy separations in the following manners. The adiabatic electron affinities (EA_{ad}) are determined by, $\text{EA}_{\text{ad}} = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})}$, zero-point corrected adiabatic electron affinities (EA_{zero}) are determined by, $\text{EA}_{\text{zero}} = E_{(\text{zero-point corrected neutral})} - E_{(\text{zero-point corrected anion})}$, the vertical electron affinities (EA_{vert}) by, $\text{EA}_{\text{vert}} = E_{(\text{optimized neutral})} - E_{(\text{anion at optimized neutral geometry})}$, and the vertical detachment energies (VDE) of the anion by, $\text{VDE} = E_{(\text{neutral at optimized anion geometry})} - E_{(\text{optimized anion})}$. The DFT descriptors, such as Fukui functions, global and local hardness or softness [10,11], also have been used for the reliable predictions in the stability of BrO_4F isomers.

2. Theory

Just like Chatterjee *et al.* [1-5] rationalized the structure-property relationship in different clays and observed that the hydroxyl groups present in the clay structure play a crucial role in the catalytic activity. We have explored the role of O and F atoms on the structure and properties of different bromine oxygen fluoide [34,35].

The hard-soft acid-base (HSAB) principles categorize the interaction between acids and bases in terms of global softness. Pearson proposed the global HSAB principle [40]. The global hardness was the second derivative of energy with respect to the number of electrons at constant temperature and external potential, which includes the nuclear field. The nonchemical meaning of the word “hardness” is resistance to deformation or change.

The global softness is the inverse of this. Pearson also pointed out a principle of maximum hardness (PMH) [41], which stated that, for a constant external potential, the system with the maximum global hardness is the most stable.

DFT-based local properties, like Fukui functions and local softness [10], have already been used for reliable predictions of electrophilic and nucleophilic reactions [1-8]. Generally, compared to a gas-phase calculation, the solvent environment alters the charge distribution of a molecule. There is an increase in the dipole moment of molecules such as water and BrF , which enhances the intrinsic reactivity of polar molecules toward nucleophilic and electrophilic attack [15]. Our aim in the current work is to explore the role of O_n chain in the structure and bonding of BrO_4F species. DFT-based local descriptors have been used for calculating the reactivity index within the helm of the HSAB principle [11-15]. It is used to determine the possible correlation between BrO_4F isomers.

In density functional theory, hardness (η) [40] is defined as:

$$\eta = (1/2)(\partial^2 E / \partial N^2)_{\nu}(r) = (1/2)(\partial \mu / \partial N)_{\nu}$$

where E is the total energy, N is the number of electrons of the chemical species, and μ is the chemical potential.

The global softness, S , is defined as the inverse of the global hardness, η :

$$S = \frac{1}{2\eta} = (\partial N / \partial \mu)_v$$

Using the finite difference approximation, S can be approximated as:

$$S = 1/(IE - EA) \quad (1)$$

where IE and EA are the first ionization energy and electron affinity of the molecule, respectively.

The Fukui function $f(r)$ is defined by [10]:

$$f(r) = [\delta \mu / \delta v(r)]_N = [\partial \rho(r) / \partial N]_v \quad (2)$$

The function f is thus a local quantity, which has different values at different points in the species, N is the total number of electrons, μ is the chemical potential, and v is the potential acting on an electron due to all nuclei present. Since $\rho(r)$ as a function of N has slope discontinuities, equation 1 provides the following three reaction indices [10]:

$$f^-(r) = [\partial \rho(r) / \partial N]_v^- \quad (\text{governing electrophilic attack})$$

$$f^+(r) = [\partial \rho(r) / \partial N]_v^+ \quad (\text{governing nucleophilic attack})$$

$$f^0(r) = (1/2)[f^+(r) + f^-(r)] \quad (\text{for radical attack})$$

In a finite difference approximation, the condensed Fukui function [16] of an atom, say x , in a molecule with N electrons is defined as:

$$f_x^+ = [q_x(N+1) - q_x(N)] \quad (\text{for nucleophilic attack}) \quad (3)$$

$$f_x^- = [q_x(N) - q_x(N-1)] \quad (\text{for electrophilic attack})$$

$$f_x^0 = [q_x(N+1) - q_x(N-1)]/2 \quad (\text{for radical attack})$$

where q_x is the electronic population of atom x in a molecule. The local softness $s(r)$ can be defined as:

$$s(r) = (\delta \rho(r) / \delta \mu)_v \quad (4)$$

Equation(3) can also be written as:

$$s(r) = [\partial \rho(r) / \partial N]_v [\partial N / \partial \mu]_v = f(r)S \quad (5)$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in the HSAB principle. Atomic softness values can easily be calculated by using equation 4, namely:

$$\begin{aligned} s_x^+(r) &= [q_x(N+1) - q_x(N)]S \\ s_x^-(r) &= [q_x(N) - q_x(N-1)]S \\ s_x^0(r) &= S[q_x(N+1) - q_x(N-1)]/2 \end{aligned} \quad (6)$$

3. Methodology

The five different DFT exchange-correlation functionals employed in this work range from generalized gradient approximation (GGA) [BLYP, BP86] to hybrid-GGA [BHLYP, B3P86, and B3LYP]. These hybrid Hartree-Fock/density functionals include: (a) Becke's half and half HF/DFT hybrid exchange functional (BH) [42] with the Lee, Yang, and Parr correlation functional (LYP) [43] (BHLYP); (b) Becke's three parameter functional [44] (B3) plus Perdew's correlation functional (P86) [45] (B3P86); (c) B3 combined with LYP functionals (B3LYP) [44,43]; (d) incorporation of Becke's 1988 exchange functional (B) [46] with Perdew's correlation functional (P86) (BP86); (e) B along with LYP (BLYP) [46,43]. The standard double- ζ plus polarization (DZP) basis set augmented with diffuse functions (DZP++) were utilized. The basis set for bromine was comprised of Ahlrichs' standard double-*spd* set plus a set of *d*-type polarization functions [$\alpha_d(\text{Br}) = 0.389$] [47] plus diffuse functions [$\alpha_s(\text{Br}) = 0.0469$ and $\alpha_p(\text{Br}) = 0.0465$]. For oxygen and fluorine, the basis sets were composed of the standard Huzinaga-Dunning [48,49] double- ζ set plus one set of polarization functions [$\alpha_d(\text{O}) = 0.85$, $\alpha_d(\text{F}) = 1.00$] augmented with one set of diffuse functions [$\alpha_s(\text{O}) = 0.08227$, $\alpha_p(\text{O}) = 0.06508$, and $\alpha_s(\text{F}) = 0.1049$, $\alpha_p(\text{F}) = 0.0826$]. The final contracted basis sets are thus designated as Br (15s12p6d/9s7p3d), O (10s6p1d/5s3p1d), and F (10s6p1d/5s3p1d). All of the molecular structures and the electron affinities have been determined using the Gaussian 03 program suite [50]. The fine integration grid (99 590) was used. All stationary point geometries were characterized by the evaluation of their harmonic vibrational frequencies at the five different levels of theory. Unless otherwise reported, the geometries in figures were found to be minima after determining the harmonic vibrational frequencies via analytical second derivatives for the corresponding stationary point structures for each function.

Besides the electron affinities, the bond dissociation energies for $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ are also determined as the difference in total energies in the following manners:

The bond dissociation energies for the neutrals refer to the reactions:



The bond dissociation energies for the anions refer to the reactions:



The natural bond orbital (NBO) analysis [51] was carried out at the B3LYP/DZP++ level for some species, corresponding Wiberg bond index (WBI) and atomic charges are obtained. Unless otherwise stated, we use the B3LYP result for molecular structures and energetics. The counterpoise (CP) method [52] was used to correct the basis set superposition error (BSSE) [7,53] using the Boys-Bernardi method in the calculation of the binding energy for the current basis. For these complexes of Lewis species, the single point calculations of the cation and anion of each molecule at the optimized geometry of the neutral molecule were also carried out to evaluate Fukui functions, global and local softness [10]. The condensed Fukui function and atomic softness were evaluated using equations 3 and 6 in Section 2. Theory, respectively. The gross atomic charges were evaluated using the technique of

Mulliken charges, due to the Br atomic charge can hardly be evaluated by using the technique of electrostatic potential (ESP) driven charges.

4. Results and Discussion

With the present five DFT methods, the optimized O-F bond length for single OF molecule ranges from 1.331 Å (BHLYP) to 1.385 Å (BLYP) (not shown). The trend of bond lengths predicted for O-F is BHLYP < B3P86 < B3LYP < BP86 < BLYP. The DZP++ B3LYP method gives the result closest to the experimental O-F bond length (r_e) of 1.3541 Å, obtained from Raman spectroscopy [18 and references cited therein]. The B3LYP method also obtain the best prediction result for dissociation energy (D_e) of OF [23] and BrO [21]. For a discussion of the reliability of B3LYP thermochemistry, see the recent work of Boese, Martin, and Handy [54]. Therefore, in the following discussion, unless otherwise stated, we use the B3LYP result for molecular structures and energetics.

For neutral BrO₄F species, the molecular chain FBr...OO...OO structure with a terminal F-Br moiety connected by OO...OO chain lies the lowest energetically. This structure in its ⁵A' state (all of the five DFT methods) or ³A' state (both BP86 and BLYP pure DFT methods) corresponds a very loose van der Waals complex between BrF...OO and O₂, possessing a binding energy of about zero and the very long Br...O (2.719-3.004 Å in ⁵A' state and 2.618, 2.719 Å in ³A' state) and (O)O...O(O) (5.220-7.095 Å in ⁵A' state, and 5.746, 6.014 Å in ³A' state) distances (not shown). It is favorable to dissociate into BrF + 2O₂ (³Σ_g⁻) or BrF + O₂ (¹Δ_g) + O₂ (³Σ_g⁻).

The FBr...OO...OO structures in ³A' state (**a**: ³A') optimized by three hybrid DFT methods (BHLYP, B3P86 and B3LYP) and in ¹A' (**b**: ¹A') (BHLYP) or ¹A (**b**: ¹A) state (with the rest four DFT methods) are reported in Figure 1. The optimized geometries for both Br- and F-terminal structures, including cis- and trans- BrOO...OOF (**c**: ¹A and **d**: ¹A), and BrOO(O)...OF (**e**: ¹A), and those of Br-hypervalent structures, O₂Br...OOF (**f**: ¹A) and FBrO₃...O (**g**: C_{3v}, ³A₁) are also displayed in Figure 1. The optimized geometries for anionic BrO₄F⁻ species, including (FBr...OO)...OO (**aa**: ⁴A') chain, and [FBr(O₂)...OO]⁻ (**ab**: ²A'), (FO...BrO₃)⁻ (**ac**: ²A') Br-hypervalent structures are shown in Figure 2. They may represent an important intermediate in atmospheric reactions.

The calculated energies (Table 1) show that the FBr...OO...OO structure in its ⁵A' state or its dissociation products (FBr...OO (³A') + O₂ (³Σ_g⁻)) lies lower than the corresponding ³A' (**a**) and ¹A' or ¹A (**b**) states by about 33 and 60 kcal/mol respectively with the B3LYP method. This state also lies much lower than the cis-, trans- BrOO...OOF (**c**: ¹A and **d**: ¹A) and BrOO₂...OF (**e**: ¹A) isomers by ca. 64, 64, and 95 kcal/mol (Table 1) respectively (B3LYP). The O₂Br...OOF (**f**: ¹A) and FBrO₃...O (**g**: C_{3v}, ³A₁) Br-hypervalent structures lie much higher than the ⁵A' state by ca. 78 and 130 kcal/mol (Table 1) respectively. With a few exceptions, the two pure DFT methods (BP86 and BLYP) predict much smaller relative energies and the bond dissociation energies than three hybrid DFT methods. All these discrepancies indicate that BrO₄F is a challenging target for DFT methods.

Figure 1. Optimized geometries of neutral BrO₄F (a-g) with DFT/DZP++ approach (bond lengths in Å, bond angles and dihedral angles in degrees). A: represents bond angle, D: represents torsion angle.

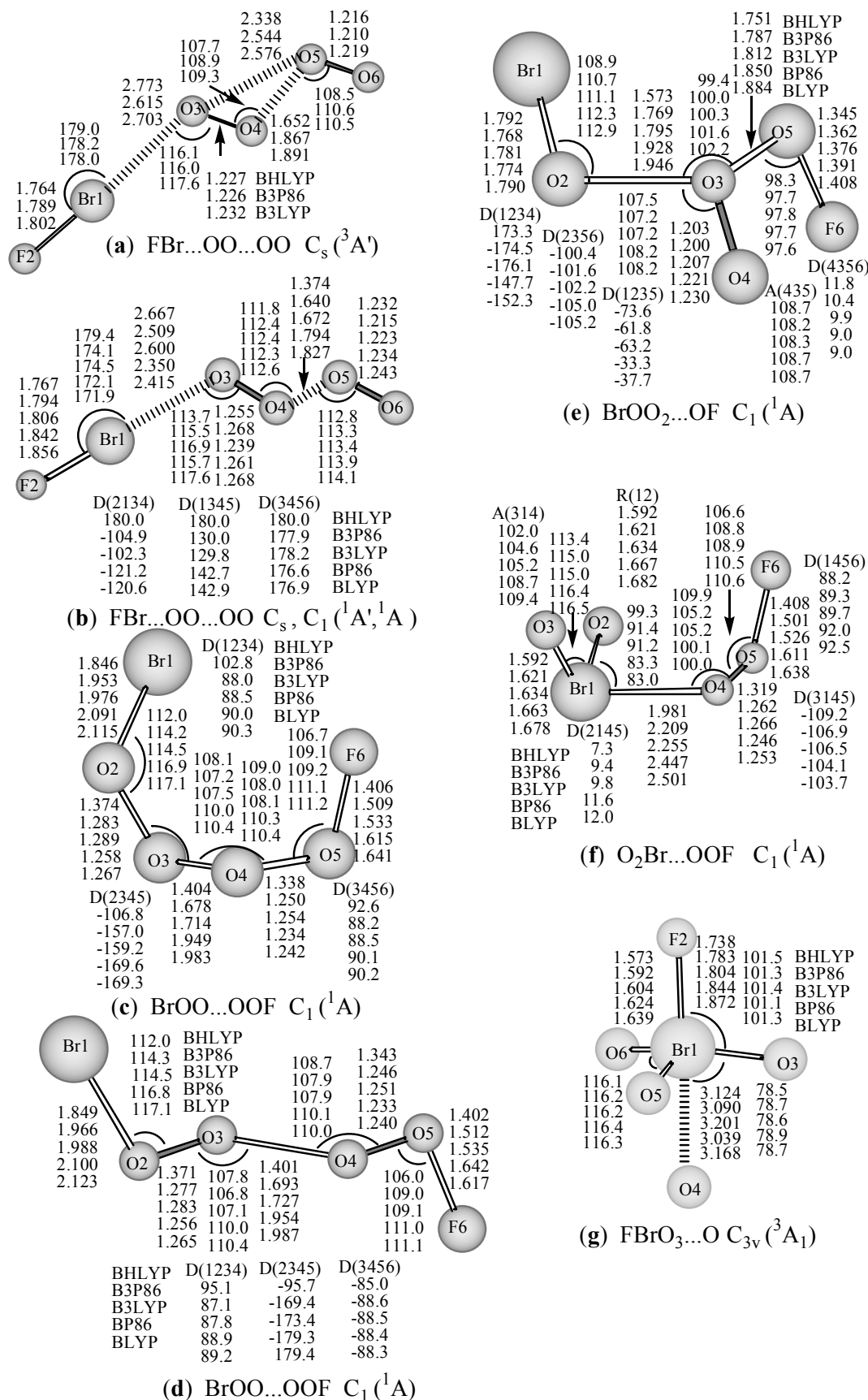


Table 1. Relative energies in kcal·mol^{−1} for BrO₄F and its dissociation products species ^a.

	BHLYP	B3P86	B3LYP	BP86	BLYP
FBr···OO···OO(⁵A'')	0.00	0.00	0.00	0.00	0.00
FBr···OO(³A'') + O₂(³Σ_g[−])^c	0.00	0.00	0.00	0.00	0.00
(a) (C_s, ³A')	56.08	31.27	33.03	--- ^b	--- ^b
(b) (C_s, ¹A')	106.42	57.41	60.41	21.72	24.59
(c) (C₁, ¹A)	88.48	60.12	64.18	31.04	34.06
(d) (C₁, ¹A)	87.86	60.49	64.22	31.31	34.97
(e) (C₁, ¹A)	136.87	91.65	94.63	60.82	62.94
(f) (C₁, ¹A)	112.37	72.28	78.33	43.66	48.31
(g) (C_{3v}, ³A₁)	134.71	123.75	129.94	118.89	124.35
FBr···OOO(¹A') + O^c	109.33	100.48	99.94	86.41	84.45
FBr···OO(³A'') + O₂(¹Δ_g)^c	43.19	39.65	39.15	38.02	38.90
OBrF(¹A') + O₃^c	100.63	67.12	70.73	47.95	51.31

^acorrected with ZPVE. ^bAt pure DFT methods (BP86 and BLYP), the triplet state of F-Br...O₂...O₂ dissociated to BrF and O₂. ^cThe bond dissociation energies corrected with BSSE. ^dBrOO is not converge with hybrid DFT methods.

As can be seen from Figure 1, for the FBr...OO...OO structure in its ³A' state, the covalent bond lengths are predicted to be 1.764-1.802 Å for the Br-F bond, and 1.227-1.232 Å for interim O-O and 1.216-1.219 Å for the terminal O-O bond, and the complex bond distances are 2.615-2.773 Å for Br...O, and 1.652-1.891 Å for (O)O...O(O) with three hybrid DFT methods. At the B3LYP level, Br-F bond length, the interim O-O and terminal O-O bond lengths in the ³A' state (**a** in Figure 1) are 1.802, 1.232, and 1.219 Å respectively, and Br...O or (O)O...O(O) complex distance is 2.703 or 1.891 Å respectively. These structure parameters are similar to those of the corresponding ¹A' state or ¹A state of (**b** in Figure 1), in which, the Br-F bond distance, the interim O-O and terminal O-O bond lengths (**b** in Figure 1) are slightly elongated (1.806, 1.239, and 1.223 Å respectively at B3LYP level), and Br...O or (O)O...O(O) complex distance is significantly shortened (2.600 or 1.672 Å respectively). The geometric and electronic structures show that the F-Br terminal moiety connected by OO...OO chain structure in ³A' (hybrid DFT methods) or in singlet state may be viewed as a van der Waals complex between BrF moiety and OO-OO covalent-like chain respectively. NBO analyses (B3LYP) show that the ³A' state possesses stronger single Br-F (WBI: 0.795 vs 0.781) and double O-O (WBI: 1.462 vs 1.436 for interim O-O; 1.524 vs 1.519 for terminal O-O) bonds than the singlet state, and that the covalent OO-OO (WBI: 0.418 vs 0.717) and complex Br...O (WBI: 0.063 vs 0.089) bonds in ³A' state are weaker than those in singlet state. Compared with the ³A'' state of FBr···OO [35], the Br-F and interim O-O bonds in ³A' state of FBr···OO-OO are slightly elongated by 0.01 Å, whereas Br...O distance is significantly shorter by 0.26 Å (B3LYP), and the terminal O-O bond distance is very similar to that in free O₂ (³Σ_g[−]) (1.194-1.245 Å) [55].

It is worthy to note that the geometries predicted using the five functionals are all similar, with small variations in bond lengths and angles. The general trend for the covalent bond lengths is BLYP > BP86 > B3LYP > B3P86 > BHLYP. According to previous studies on geometries of BrOF_n/BrOF_n[−], FBrO₂/FBrO₃, BrClF_n/BrClF_n[−] and BrF_n species [34,35,37,56], the hybrid DFT methods (BHLYP,

B3P86 or B3LYP method) are excellent methods for the prediction of covalent bond lengths. The B3LYP method taking the median position may be regarded as a compromise between the reliabilities of geometry and thermochemical parameter predictions. This order coincides with that predicted for the FO molecule [25] where comparison with experiment indicates the B3LYP method to be the most accurate in prediction of geometry, and for BrO in predictions of bond dissociation and adiabatic electron affinity (EA_{ad}) [21].

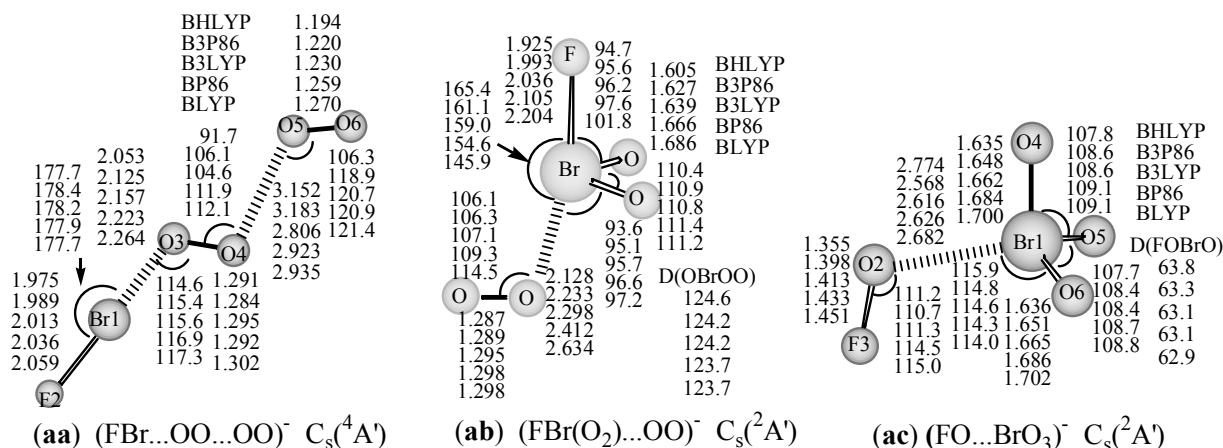
The attachment of an electron to $FBr...OO...OO$ complex, results in the $^4A'$ ground state for anion (**aa**: $^4A'$ in Figure 2). As might be expected, this structure is more stable than other anionic BrO_4F^- Br-hypervalent structures (**ab**: $^2A'$ and **ac**: $^2A'$ in Figure 2) by 32 and 78 kcal/mol at B3LYP/DZP++ level. The covalent bond lengths are predicted to be 1.975–2.059 Å for the Br-F bond, and 1.284–1.302 Å for interim O-O and 1.194–1.270 Å for the terminal O-O bond, and the complex bond distances are 2.053–2.264 Å for Br...O, and 2.806–3.183 Å for $(O)O\cdots O(O)$ in the $^4A'$ state of BrO_4F^- . Comparison with the similar neutral isomer shows that there is a substantial change in geometry between neutral $^3A'$ state and anionic $^4A'$ state. The Br-F bond (2.013 Å at B3LYP level), the interim O-O bond (1.295 Å) and Br...O bond (2.157 Å) in anionic $^4A'$ state are analogous to those of $(FBr-OO)^-$ (2.038 Å for Br-F, 1.302 Å for O-O, and 2.135 Å for Br...O) [35]; the terminal O-O bond in the $^4A'$ state of BrO_4F^- (1.230 Å) is similar to that of free O_2 (1.219 Å at B3LYP level) [55]; the $(O)O\cdots O(O)$ distance of 2.806 Å in anionic BrO_4F^- is substantially longer than the corresponding $(O)O\cdots O(O)$ distance (1.891 Å) in $^3A'$ state of neutral BrO_4F . Thus, this BrO_4F^- structure in $^4A'$ state could be regarded as a van der Waals complex between $(FBr-OO)^-$ [35] and O_2 ($^3\Sigma_g^-$) due to suitable Br...O and $(O)O\cdots O(O)$ bonding distances, and the high negative charge of $FBr-OO$ moiety (near to -1 from NBO analysis). Neither theoretical nor experimental values of BrO_4F/BrO_4F^- are available for comparison. For this structure in its doublet $^2A'$ state, the results of all five DFT methods are suspect due to the large spin contamination, with $\langle S^2 \rangle = 1.77$ or 1.76.

For the cis- and trans- $BrOO...OOF$ (**c**: 1A and **d**: 1A in Figure 1) structures, the bond lengths are calculated to be 1.846–2.123 Å for the Br-O bond (that in cis-form tiny shorter than in trans-like), 1.402–1.642 Å for the F-O bond, 1.401–1.987 Å for the central single O–O bond, and 1.233–1.374 Å for outer O–O bonds connected by Br and F. In the cis- $BrOO...OOF$, the $O...OO$ fragment nearly in a planar, both BrO and FO bonds are almost perpendicular to this planar, however, in the trans- $BrOO...OOF$, the $OO...OO$ chain nearly in a planar, the BrO and FO bonds are also almost perpendicular to this planar. At B3LYP level, both $BrOO...OOF$ isomers nearly possess the same stability. This $BrOO...OOF$ conformation could be viewed as a complex comprising of unstable BrOO and FOO molecules, furthermore, the DFT methods predict it thermodynamic instability with respect to dissociation into $BrOO + FOO$ (not shown).

For the $BrOO_2...OF$ (**e**: 1A) structures, the bond lengths are calculated to be 1.768–1.792 Å for the Br-O bond, 1.345–1.408 Å for the F-O bond, 1.200–1.230 Å for the central double O–O bond and 1.573–1.946 Å, 1.7514–1.884 Å for outer single O–O bonds connected by Br and F, respectively. At B3LYP level, the Br-O (1.781 Å) or F-O (1.376 Å) bond is slightly longer than that in BrO [21] or FO [25]. Thus, this $BrOO_2...OF$ (**e**: 1A) structures could be regarded as a complex comprising of simple BrO, O_2 and FO molecules. The hybrid DFT methods predict it thermodynamic instability with respect to dissociation into $BrO + O_2 + OF$ (not shown), whereas the pure DFT methods predict the reaction

energy of about 10 (BP86) and 6 kcal/mol (BLYP) for $\text{BrOO}_2\cdots\text{OF}$ (**e**: ^1A) $\rightarrow \text{BrO} + \text{O}_2 + \text{OF}$ (not shown).

Figure 2. Optimized geometries of anionic BrO_4F^- (**aa-ac**) with DFT/DZP++ approach (bond lengths in Å, bond angles and dihedral angles in degrees). A: represents bond angle, D: represents torsion angle.



For Br-hypervalent structures: $\text{O}_2\text{Br}\cdots\text{OOF}$ (**f**: ^1A), the bond lengths are predicted to be 1.592–1.682 Å for $\text{Br}-\text{O}_{\text{term}}$ (with an oxygen atom at the terminal position), 1.981–2.501 Å for $\text{Br}-\text{O}_{\text{mid}}$ (with O atom at the middle position), and 1.246–1.319 Å for O–O, and 1.408–1.638 Å for F–O. The predicted $\text{Br}-\text{O}_{\text{term}}$ length is comparable to that of OBrO (1.649 Å) [21], F–O or O–O bond distances are slightly shorter or longer than those in FOO (1.649 or 1.200 Å) [18]. This structure could be thought as a complex between BrO_2 and FOO . Likewise, the hybrid DFT methods predict it thermodynamic instability with respect to dissociation into $\text{BrO}_2 + \text{FOO}$ (not shown), and the pure DFT methods predict the dissociation energy of $\text{O}_2\text{Br}\cdots\text{OOF}$ (**f**: ^1A) $\rightarrow \text{BrO}_2 + \text{FOO}$ reaction is about 2.3 (BP86) and 0.5 kcal/mol (BLYP) respectively (not shown).

For the rare Br(VII) $\text{FBrO}_3\cdots\text{O}$ (**g**: $\text{C}_{3v}, ^3\text{A}_1$) complex between FBrO_3 and O atom, the bond lengths are predicted to be 1.573–1.639 Å for Br–O, 1.738–1.832 Å for Br–F, and 3.039–3.168 Å for Br $\cdots$ O. At B3LYP level, Br–O bond long is 1.604 Å, analogous to that in BrO_4^- (1.603 Å) [21] or BrO_3F_2^- (1.601 Å) [31], and longer than that in FBrO_3 (1.582 Å) [35], however, significantly shorter than that in BrO_3^- (1.648 Å) [21]. The Br–F bond length is 1.804 Å, being significantly shorter than that in BrO_3F_2^- (1.872 or 1.849 Å) [31], while substantially longer than that in FBrO_3 (1.708 Å) [35]. $\angle\text{FBrO}$ and $\angle\text{OBrO}$ angles are 101.4 and 116.2° respectively, slightly narrower than those in FBrO_3 theoretically (101.9 and 115.9) or experimentally (103.3 and 114.9°) [27]. Generally, the predicted lengths are comparable to those of FBrO_3 (C_{3v}) and BrO_3F_2^- anion [31]. The DFT methods predict the dissociation energy of $\text{FBrO}_3\cdots\text{O}$ (**g**: $\text{C}_{3v}, ^3\text{A}_1$) $\rightarrow \text{FBrO}_3$ (C_{3v}) + O reaction is about 1 kcal/mol (Table 1), demonstrating that this Br(VII) $\text{FBrO}_3\cdots\text{O}$ (**g**: $\text{C}_{3v}, ^3\text{A}_1$) hypervalent structure is bound for dissociation to FBrO_3 and O.

The corresponding anion eventually to dissociation into $\text{FBr}(\text{O}_2)\cdots\text{OO}$ (**ab**: $^2\text{A}'$) complex structure, Br–F and Br–O bonds are elongated to be 2.036 and 1.639 Å (B3LYP), the Br $\cdots$ O complex distance and O–O bond length are about 2.3 and 1.30 Å. The DFT methods predict the dissociation energy of

$\text{FBr}(\text{O}_2)^-\dots\text{OO}(\mathbf{ab}: {}^2\text{A}') \rightarrow \text{BrF}^- + \text{O}_2({}^3\Sigma_g^-) + \text{O}_2({}^1\Delta_g)$ reaction being in the range of 7-48 kcal/mol, the BHLYP result is too small (7 kcal/mol). This is not unexpected, given the large fraction of exact exchange in the BHLYP method [57]. For the global minimum $\text{FBr}\dots\text{OO}\dots\text{OO}$ anion ($\mathbf{aa}: {}^4\text{A}'$), the predictions of five different DFT methods for the dissociation energies for $\mathbf{aa}$ to dissociate to its components [$\text{FBr}\dots\text{OO}({}^2\text{A}') + \text{O}_2$, $\text{FBr}\dots\text{OO}({}^3\text{A}') + \text{O}_2^-$, or $\text{BrF}^- + 2\text{O}_2({}^3\Sigma_g^-)$] show the same trend, i.e. the pure DFT (BP86 and BLYP) methods predict higher dissociation energies than the hybrid DFT methods, and the BHLYP result is the smallest.

For the higher-lying hypervalent anionic $(\text{FO}\dots\text{BrO}_3)^-$ complex structure ($\mathbf{ac}: {}^2\text{A}'$), the bond lengths are predicted to be 1.635-1.702 Å for Br-O bonds, 1.355-1.451 Å for F-O bond, 1.355-1.451 Å for F-O bond, and 2.568-2.774 Å for Br...O complex bond. The theoretical dissociation energies for $(\text{FO}\dots\text{BrO}_3)^- \rightarrow \text{BrO}_3^-(\text{C}_{3v}) + \text{FO}$ is in the range of 2.8-17.9 kcal/mol (Table 2). Likewise, the pure DFT methods predict higher dissociation energies, and the BHLYP result is the lowest.

Table 2. Relative energies (corrected with ZPVE) in kcal mol⁻¹ for the BrO_4F^- species ^a.

	BHLYP	B3P86	B3LYP	BP86	BLYP
$\mathbf{aa} (\text{C}_s, {}^4\text{A}')$	0.00	0.00	0.00	0.00	0.00
$\mathbf{ab} (\text{C}_s, {}^2\text{A}')$	44.67	27.77	32.06	22.02	25.84
$\mathbf{ac} (\text{C}_s, {}^2\text{A}')$	89.41	74.36	78.47	69.67	73.64
$\text{FBr}\dots\text{OOO}({}^2\text{A}') + \text{O}^b$	62.73	72.17	71.24	78.52	77.23
$\text{FBr}\dots\text{OO}({}^2\text{A}') + \text{O}_2^b$	1.02	1.49	1.38	4.42	4.90
$\text{OBrF}^- + \text{O}_3^b$	72.04	59.70	60.46	52.44	54.10
$\text{FBr}\dots\text{OOO}({}^1\text{A}') + \text{O}^b$	143.20	137.42	135.97	127.36	126.87
$\text{FBr}\dots\text{OO}({}^3\text{A}') + \text{O}_2^b$	50.96	60.66	57.87	69.20	67.16
$\text{OBrF}({}^1\text{A}') + \text{O}_3^b$	92.18	79.32	80.61	75.51	76.23
$\text{BrF}^- + 2\text{O}_2({}^3\Sigma_g^-)^b$	-1.39	11.42	9.06	20.79	19.59
$\text{BrO}_3^- + \text{OF}^b$	92.59	86.40	90.39	87.94	92.27

^a corrected with ZPVE. ^b The bond dissociation energies corrected with BSSE.

Generally, the theoretical dissociation energies (D_e) for $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ species can be evaluated from the data in Tables 1 and 2. For the anionic BrO_4F^- species, all of five DFT methods predict almost consistent relative energies and bond dissociation energies, with the exception of the lowest BHLYP results (Table 2) (vide supra). In contrast, for the neutral BrO_4F species (Table 1), the relative energies and bond dissociation energies predicted by BHLYP method are nearly the biggest. It is noted that BHLYP method perform poorly for bond-breaking process [57] due to the large (50%) contribution from Hartree-Fock or exact exchange. Based on the previous studies of the BrO_n species [21] and the anionic BrO_4F^- species (vide supra), the B3LYP methods should predict reasonable dissociation energies and relative energies, however, caution is urged because of the complex of BrO_4F ternary system.

At B3LYP level, for the lowest energies species, the theoretical bond dissociation energies for neutral BrO_4F refer to the reactions: $\text{BrO}_4\text{F} \rightarrow \text{BrO}_{4-m}\text{F} + \text{O}_m$ ($m = 1-4$). For $\text{BrO}_4\text{F} \rightarrow \text{BrO}_2\text{F}({}^3\text{A}') + \text{O}_2$, the theoretical reaction energies (ca. zero) are much smaller than those of $\text{BrO}_4\text{F} \rightarrow \text{BrO}_3\text{F}({}^1\text{A}') + \text{O}$ (range from 84 to 109 kcal/mol, about 100 kcal/mol at B3LYP level) and $\text{BrO}_4\text{F} \rightarrow \text{BrOF}$

($^1A'$) + O₃ (range from 48 to 101 kcal/mol, ca. 71 kcal/mol at B3LYP level), indicating the dissociation reaction is favored, which is consistent with the FBr...O₂...O₂ complex structure.

The most reliable B3LYP method predicts the dissociation energy (D_e) for F-Br...O₂...O₂ ($^5A'$) → BrF + 2O₂ and (F-Br...O₂...O₂)⁻ ($^4A'$) → BrF⁻ + 2O₂ are only 0.0 and 9.1 kcal/mol, respectively (Tables 1 and 2), suggesting a weak van der Waals interaction between the BrF or BrF⁻ and O₂ moieties.

For the anionic BrO₄F⁻ species, the D_e of BrO₄F⁻ → BrO_{4-m}F⁻ + O_m and BrO₄F⁻ → BrO_{4-m}F + O_m⁻ are predicted (Table 2). The bond dissociation energies for BrO₄F⁻ → BrO₂F⁻ + O₂ are smaller positive values, from 1.0 to 1.5 kcal/mol for three hybrid DFT methods and 4.4 or 4.9 kcal/mol for BP86 or BLYP (two pure DFT) methods. The D_e values predicted by BHLYP method are too low to be reliable. The D_e value of 1.4 kcal/mol predicted by B3LYP is much smaller than those of BrO₄F⁻ → BrO₃F⁻ + O (71 kcal/mol) and BrO₄F⁻ → OBrF⁻ + O₃ (60 kcal/mol).

For BrO₄F⁻ → BrO_{4-m}F + O_m⁻ reactions, the higher bond dissociation energies are predicted, the D_e value (58 kcal/mol) of BrO₄F⁻ → BrO₂F + O₂⁻ is also smaller than those of BrO₄F⁻ → BrO₃F + O⁻ (136 kcal/mol) and BrO₄F⁻ → OBrF + O₃⁻ (81 kcal/mol), and demonstrating that complex BrO_nF [34,35] species have higher electron affinities than the free O_m species [55]. For the challenging BrO_mF/BrO_mF⁻ (m = 1-4) species, minima on PES were found with all of DFT methods employed. However, the thermodynamic stabilities decrease with n (vide supra).

The EA_{ad} for FBr-O₂-O₂ (a: $^3A' \leftarrow aa: ^4A'$) are predicted to be 4.95 eV(BHLYP), 4.97 eV(BP86), and 4.52 eV(B3LYP), zero-point corrected EA_{ad} (EA_{zero}) is only increased about 0.05 eV. At B3LYP level, EA_{zero} is 4.57 eV, larger than those of FBr-OOO [35] and FBrO [34] by about 0.1 and 1.9 eV respectively, and much smaller than those of FBr-OO by 1.3 eV (B3LYP). Those with odd n (n = 1 and 3, closed shell) have smaller EAs than those of species for the even number of n (n = 2 and 4), which are open-shell triplet state. The EA_{vert} values range from 2.13 to 3.55 eV. The range of VDE is from 4.49 to 4.98 eV. No experimental data are available.

The harmonic vibrational frequencies and IR active intensities of BrO₄F/BrO₄F⁻ species predicted by B3LYP method are available in Tables 3 and 4. For triplet state FBr...O₂...O₂ (**a**) (C_s, $^3A'$), the calculated infrared spectrum is characterized by three strong bands around 1561 (terminal O-O symmetri stretch(s.s.)), 1440 (middle O-O s.s.), 628 cm⁻¹ (F-Br s.s.), all other modes give rise to weak intensities. For singlet state FBr...OOOO (**b**) (C₁, 1A), the bands of ca. 1508 (terminal O-O s.s.), 1391 (middle O-O s.s.), and 620 cm⁻¹ (F-Br s.s.) possess the stronger intensities. For BrOO...OOF chain structures (**c**) and (**d**), the predicted infrared spectrum are characterized by three stronger bands around 1223, 1376 (F-connected O-O s.s.), 1107, 1276 (Br-connected O-O s.s.), and 720, 667 cm⁻¹ (F-O-O bend), respectively, the rest modes yield weak intensities. For BrOO2...OF structure (**e**), four bands around 1209, 934, 862, and 718 cm⁻¹ exist the stronger intensities, the corresponding modes are O-O (O2) s.s., F-O s.s., Br-O s.s., and O...O stretch.

For O₂Br...OOF structure (**f**), four bands around 1529, 1055, 732, and 618 cm⁻¹ possess the stronger intensities, the corresponding modes are O-O stretch, OBrO asymmetric bend, OBrO symmetric bend, and FOO bend. For the highest symmetric Br(VII) FBrO₃...O (**g**), theoretical infrared spectrum are characterized by the stronger bands around θ: 955 cm⁻¹ (BrO₃ asymmetric stretch (a.s.)); η: 864 cm⁻¹ (BrO₃ symm.bend); ζ: 567 cm⁻¹ (F-Br s.s.); ε: 364 cm⁻¹ (OBrO in the planar bend); δ: 345 cm⁻¹ (OBrO out of planar bend), the harmonic vibrational frequencies of BrO₃ radical are larger than the

corresponding BrO_3^+ [32] (966, 850, 329, and 231 cm^{-1}). For anionic quartet state $\text{FBr}\dots\text{OO}\dots\text{OO}$ (**aa**) ($\text{C}_s, {}^4\text{A}'$) species, four bands around 1532, 1226, 383, and 227 cm^{-1} possess the stronger intensities. For anionic hypervalency structure $[\text{FO}\dots\text{Br}(\text{O})\text{O}_2]^-$ (**ac**) ($\text{C}_s, {}^2\text{A}'$), four bands around 957, 812, 805, 789 cm^{-1} possess the stronger intensities.

Table 3. Predicted total energies(E_{total}) in hartree, zero-point vibrational energies (ZPE) in kcal mol^{-1} , and harmonic vibrational frequencies (Freq) in cm^{-1} and the infrared intensities (in parentheses, in $\text{km}\cdot\text{mol}^{-1}$) for the minimum-energy BrO_4F (**a**, **b**, **c**, **d**, and **e**) structures at the B3LYP/DZP++ level.

Isomers	a ($\text{C}_s, {}^3\text{A}'$)	b ($\text{C}_1, {}^1\text{A}$)	c ($\text{C}_1, {}^1\text{A}$)	d ($\text{C}_1, {}^1\text{A}$)	e ($\text{C}_1, {}^1\text{A}$)
E_{total}	-2974.61676	-2974.57337	-2974.56896	-2974.56840	-2974.54599
ZPE	7.37	7.88	8.53	8.22	8.05
Freq	$\omega_1(\text{a}'') 27 (<1)$ $\omega_2(\text{a}') 35 (1)$ $\omega_3(\text{a}'') 67 (<1)$ $\omega_4(\text{a}') 68 (5)$ $\omega_5(\text{a}'') 96 (1)$ $\omega_6(\text{a}') 102 (2)$ $\omega_7(\text{a}') 206 (4)$ $\omega_8(\text{a}') 276 (10)$ $\omega_9(\text{a}') 628 (132)$ $\omega_{10}(\text{a}') 650 (<1)$ $\omega_{11}(\text{a}') 1440 (643)$ $\omega_{12}(\text{a}') 1561 (110)$	$\omega_1 13 (<1)$ $\omega_2 61 (1)$ $\omega_3 81 (3)$ $\omega_4 97 (7)$ $\omega_5 110 (2)$ $\omega_6 225 (1)$ $\omega_7 292 (5)$ $\omega_8 345 (3)$ $\omega_9 620 (142)$ $\omega_{10} 766 (<1)$ $\omega_{11} 1393 (529)$ $\omega_{12} 1508 (278)$	$\omega_1 28 (<1)$ $\omega_2 97 (1)$ $\omega_3 175 (3)$ $\omega_4 249 (7)$ $\omega_5 287 (3)$ $\omega_6 367 (13)$ $\omega_7 501 (44)$ $\omega_8 546 (33)$ $\omega_9 664 (60)$ $\omega_{10} 720 (74)$ $\omega_{11} 1107 (105)$ $\omega_{12} 1223 (112)$	$\omega_1 24 (<1)$ $\omega_2 59 (1)$ $\omega_3 103 (<1)$ $\omega_4 201 (0)$ $\omega_5 252 (4)$ $\omega_6 281 (36)$ $\omega_7 444 (28)$ $\omega_8 496 (63)$ $\omega_9 571 (1)$ $\omega_{10} 667 (172)$ $\omega_{11} 1276 (162)$ $\omega_{12} 1376 (69)$	$\omega_1 79 (<1)$ $\omega_2 98 (<1)$ $\omega_3 133 (0)$ $\omega_4 211 (14)$ $\omega_5 247 (2)$ $\omega_6 338 (16)$ $\omega_7 451 (3)$ $\omega_8 502 (32)$ $\omega_9 718 (148)$ $\omega_{10} 862 (86)$ $\omega_{11} 934 (93)$ $\omega_{12} 1209 (161)$

Table 4. Predicted total energies(E_{total}) in hartree, zero-point vibrational energies (ZPE) in kcal mol^{-1} , and harmonic vibrational frequencies (Freq) in cm^{-1} and the infrared intensities (in parentheses, in km mol^{-1}) for the minimum-energy $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ (**f**, **g/aa**, **ac**) structures at the B3LYP/DZP++ level.

Isomers	f ($\text{C}_1, {}^1\text{A}$)	g ($\text{C}_{3v}, {}^3\text{A}_1$)	aa ($\text{C}_s, {}^4\text{A}'$)	ac ($\text{C}_s, {}^2\text{A}'$)
E_{total}	-2974.52034	-2974.46217	-2974.78297	-2974.65675
ZPE	8.47	7.28	6.22	7.03
Freq	$\omega_1 41 (<1)$ $\omega_2 104 (0)$ $\omega_3 110 (1)$ $\omega_4 231 (4)$ $\omega_5 246 (5)$ $\omega_6 283 (4)$ $\omega_7 438 (30)$ $\omega_8 535 (5)$ $\omega_9 618 (6)$ $\omega_{10} 732 (42)$ $\omega_{11} 1055 (131)$ $\omega_{12} 1529 (360)$	$\omega_1(\text{e}) \alpha 39 (<1)$ $\omega_2(\text{a}_1) \beta 66 (<1)$ $\omega_3(\text{e}) \gamma 269 (<1)$ $\omega_4(\text{a}_1) \delta 345 (25)$ $\omega_5(\text{e}) \epsilon 364 (30)$ $\omega_6(\text{a}_1) \zeta 567 (144)$ $\omega_7(\text{a}_1) \eta 864 (21)$ $\omega_8(\text{e}) \theta 955 (106)$	$\omega_1(\text{a}') 13 (<1)$ $\omega_2(\text{a}'') 16 (<1)$ $\omega_3(\text{a}'') 34 (<1)$ $\omega_4(\text{a}') 49 (3)$ $\omega_5(\text{a}') 102 (5)$ $\omega_6(\text{a}') 151 (29)$ $\omega_7(\text{a}'') 181 (7)$ $\omega_8(\text{a}') 227 (45)$ $\omega_9(\text{a}') 383 (636)$ $\omega_{10}(\text{a}') 437 (25)$ $\omega_{11}(\text{a}') 1226 (116)$ $\omega_{12}(\text{a}') 1532 (1291)$	$\omega_1(\text{a}'') 31 (1)$ $\omega_2(\text{a}') 56 (3)$ $\omega_3(\text{a}'') 77 (4)$ $\omega_4(\text{a}') 90 (2)$ $\omega_5(\text{a}') 200 (8)$ $\omega_6(\text{a}'') 327 (14)$ $\omega_7(\text{a}') 327 (14)$ $\omega_8(\text{a}') 390 (63)$ $\omega_9(\text{a}') 789 (100)$ $\omega_{10}(\text{a}') 805 (174)$ $\omega_{11}(\text{a}') 812 (181)$ $\omega_{12}(\text{a}') 957 (397)$

Isodesmic reactions, which have been typically used to obtain the heats of formation for many molecules, are those in which the reactants and products contain the same types of bonds, i.e., the number of bonds broken and formed is conserved [58]. An isodesmic reaction scheme requires that the heats of formation of all the molecules involved in the reaction to be known with the exception of the heat of formation of the particular isomer. Because of this property, errors in the energy that might occur due to defects in the basis set and electron correlation cancel, to a large extent. The isodesmic scheme used here is $\text{BrOOOOOF} + 4\text{HOH} \rightarrow 3\text{HOOH} + \text{HOBr} + \text{HOF}$. During the calculation of the heat of formation of BrOOOOOF using the isodesmic scheme, literature values for the heats of formation of HOH ($-57.10 \text{ kcal mol}^{-1}$) [59], HOOH ($-31.02 \text{ kcal mol}^{-1}$) [59], and HOBr ($-10.93 \text{ kcal mol}^{-1}$) [60], HOF ($-22.47 \text{ kcal mol}^{-1}$) [61], were used. Using these results we were able to calculate the heats of reaction. For cis BrOOOOOF (**c**), the heat of formation is predicted to be 50 kcal mol^{-1} at B3LYP level of theory (Table 5). Using the relative energies (Table 1) along with the heat of formation of BrOOOOOF (**c**), we obtained a value of 19 kcal mol^{-1} for FBrOOOOO(**a**), 83 kcal mol^{-1} for BrOO2...OF (**e**), 64 kcal mol^{-1} for O₂Br...OOF (**f**), and $116 \text{ kcal mol}^{-1}$ for FBrO₃...O (**g**) (shown in Table 6). To further assess these results, we have listed all five DFT methods heats of formation of the isomers in Table 6. At present, there are no experimental measurements to which be mainly due to the incompleteness of the basis sets and only partial allowance for electron correlation.

Table 5. Isodesmic heats of reaction (kcal mol^{-1}) and heats of formation of BrOOOOOF (**c**).

Levels	Total energies (hartrees)				BrOOOOOF c (C_{1v} , ^1A)	$\Delta H_{\text{r} \rightarrow 0}^0$	$\Delta H_{\text{f},0}^0$ (BrOOOOOF)
	HOH	HOBr	HOOH	HOF		BrOOOOOF + 4H ₂ O → 3H ₂ O ₂ + HOBr + HOF	
BHLYP	-76.40988	-2649.83736	-151.51249	-175.50871	-2974.29785	38.66	63.28
B3P86	-76.62947	-2650.88786	-151.91207	-175.90318	-2976.08610	52.80	49.14
B3LYP	-76.45274	-2649.92233	-151.59656	-175.59224	-2974.56896	51.98	49.96
BP86	-76.45287	-2650.17532	-151.60450	-175.59915	-2974.89229	76.51	24.74
BLYP	-76.43467	-2649.91747	-151.57898	-175.58312	-2974.61332	75.55	25.70

Table 6. Heats of formation (kcal mol^{-1}) of BrO₄F isomers.

	a	b	c	d	e	f	g
BHLYP	30.88	81.19	63.28	62.65	63.28	62.65	109.51
B3P86	20.30	46.44	49.14	49.51	83.45	61.30	112.77
B3LYP	18.81	46.49	49.96	50.00	82.94	64.11	115.72
BP86	--- ^a	15.41	24.74	25.01	56.76	37.36	112.59
BLYP	--- ^a	16.23	25.70	25.71	56.54	39.95	116.00

^aAt pure DFT methods (BP86 and BLYP), the triplet state of F-Br...O₂...O₂ dissociated to BrF and O₂.

For these complexes of Lewis acid (BrF) and base (lone pair O_m chains), we treated as a local version of the hard and soft acid base (HSAB) principle [40]. The DFT-based local reactivity descriptors such as the global or local softness or hardness, condensed Fukui functions can be used to explain the stability of isomers. The predicted global hardness (η) and softness (GS) for the minimum-

energy BrO₄F structures (**a**, **b**, **c**, **d**, **e**, **f**, and **g** isomers) with five DFT methods are shown in Tables 7 and 8 respectively. The local softness (S_x^+ and S_x^-), and ratios of them (S_x^-/S_x^+) for the minimum BrO₄F structures (**a**, **b**, **c**, **d**, **e**, **f**, and **g** isomers) at the B3LYP/DZP++ level are tabulated in Table 9. According the Pearson's PMH suggestion [41], the Br(VII) structure (**g**) FBrO₃...O in this work has the largest global hardness (Table 7), and smallest global softness (Table 8), thus triplet state FBrO₃...O structure is the most stable isomer. For BrO₄F isomers, the maximum value (from 5.1 to 8.2, at B3LYP/DZZ++ level, as 8.2) of global hardness (Table 7) set in the highest symmetric Br(VII) FBrO₃...O structure (**g**), whereas the minimum value (from 2.9 to 3.2) of hardness assign to singlet BrOO...OOF isomer (**b**), inversely, the isomers (**g**) or (**b**) possesses the smallest or largest global softness (Table 8), respectively, namely, from 0.06 to 1.0, or from 0.16 to 0.17. For Br in the different isomers presents almost either the largest or smallest S_x^-/S_x^+ values (Table 9), corresponding to different bonds stabilities. An important finding from this investigation is that Br may reveal the flexibility in which the bromine atom shares valence electrons and orbitals to form a variety of hypervalent species, even the extend hypervalent system.

Table 7. Global hardness Approximated as: $\eta = 1/2(IE - EA)$ of BrO₄F isomers.

	a	b	c	d	e	f	g
BHLYP	4.7887	3.0850	4.9960	4.9734	4.1040	4.6173	6.0183
B3P86	4.1283	3.1846	4.3096	4.2192	3.7400	4.0823	5.0613
B3LYP	4.1415	2.8950	4.1995	4.1144	3.5957	3.9306	8.2104
BP86	--- ^a	3.1694	4.8052	3.6550	3.5028	3.8778	6.9996
BLYP	--- ^a	3.1108	3.6132	3.5698	3.4107	3.7634	7.0271

^bAt pure DFT methods (BP86 and BLYP), the triplet state of F-Br...O₂...O₂ dissociated to BrF and O₂.

Table 8. Global softness approximated as: $GS = 1/(2\eta) = 1/(IE - EA)$ of BrO₄F isomers.

	a	b	c	d	e	f	g
BHLYP	0.1044	0.1621	0.1001	0.1005	0.1218	0.1083	0.0831
B3P86	0.1211	0.1570	0.1160	0.1185	0.1337	0.1225	0.0988
B3LYP	0.1207	0.1727	0.1191	0.1215	0.1391	0.1272	0.0609
BP86	--- ^a	0.1578	0.1041	0.1368	0.1427	0.1290	0.0714
BLYP	--- ^a	0.1607	0.1384	0.1401	0.1466	0.1329	0.0712

^bAt pure DFT methods (BP86 and BLYP), the triplet state of F-Br...O₂...O₂ dissociated to BrF and O₂.

Table 9. Predicted global softness (GS), local softness (S_x^+ and S_x^-), and ratio of them for the BrO₄F (**a**, **b**, **c**, **d**, **e**, **f**, and **g**) isomers.

Species	GS	atom	S_x^+	S_x^-	S_x^0	S_x^-/S_x^+
a	0.1207	Br1	0.0139	0.0524	0.0332	3.7739
		F2	0.0091	0.0173	0.0132	1.8959
		O3	0.0321	0.0097	0.0209	0.3024
		O4	0.0191	0.0096	0.0144	0.5014
		O5	0.0136	0.0114	0.0125	0.8398
		O6	0.0329	0.0203	0.0266	0.6171
b	0.1727	Br1	0.0329	0.0695	0.0516	2.1350
		F2	0.0152	0.0248	0.0202	1.6460
		O3	0.0391	0.0240	0.0317	0.6206
		O4	0.0303	0.0089	0.0196	0.2964
		O5	0.0188	0.0077	0.0133	0.4142
		O6	0.0363	0.0359	0.0363	0.9989
c	0.1191	Br1	0.0758	0.0529	0.0643	0.6976
		O2	0.0025	0.0143	0.0084	5.6573
		O3	0.0120	0.0102	0.0111	0.8584
		O4	0.0067	0.0100	0.0083	1.5076
		O5	0.0122	0.0178	0.0150	1.4537
		F6	0.0100	0.0139	0.0119	1.4003
d	0.1215	Br1	0.0771	0.0540	0.0656	0.7007
		O2	0.0021	0.0144	0.0083	6.7342
		O3	0.0116	0.0102	0.0109	0.8789
		O4	0.0064	0.0094	0.0079	1.4708
		O5	0.0113	0.0165	0.0139	1.4627
		F6	0.0131	0.0170	0.0150	1.3029
e	0.1391	Br1	0.0451	0.0634	0.0542	1.4053
		O2	0.0212	0.0243	0.0228	1.1459
		O3	0.0057	0.0027	0.0042	0.4809
		O4	0.0294	0.0225	0.0260	0.7664
		O5	0.0243	0.0137	0.0190	0.5635
		F6	0.0133	0.0124	0.0128	0.9313
f	0.1272	Br1	0.0343	0.0174	0.0259	0.5084
		O2	0.0242	0.0234	0.0238	0.9666
		O3	0.0256	0.0341	0.0298	1.3307
		O4	0.0164	0.0168	0.0166	1.0268
		O5	0.0122	0.0179	0.0150	1.4651
		F6	0.0146	0.0176	0.0161	1.2120
g	0.0609	Br1	0.0094	-0.0046	0.0024	-0.4827
		F2	0.0072	0.0069	0.0070	0.9580
		O3	0.0065	-0.0008	0.0029	-0.1171
		O4	0.0249	0.0608	0.0429	2.4447

5. Conclusions

The structures, electron affinities and bond dissociation energies of $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ species have been studied with five DFT methods. The B3LYP method is the most reliable method for predicting the geometry and electron affinities for this ternary species. The EA_{ad} value predicted by the B3LYP method is 4.52 eV for BrO_4F . The EA_{ad} values for OBrF [34], FBrOO , and FBrOOO [35] species are 3.64, 5.83 and 4.43 eV, respectively. and close to those of other interhalogen compounds, such as BrClF_n and BrF_n [37,56]. Those with odd n ($n = 1$ and 3, closed shell) have smaller EA_{ad} than those of even n ($n = 2$ and 4) species, which are open-shell triplet state. These substantial electron affinities suggest that the corresponding anion may have the lifetimes as independent species under atmospheric conditions.

Similar to the case of the electron affinities, the hybrid DFT methods especial B3LYP predict the discrepant values of bond dissociation energies for $\text{BrO}_4\text{F}/\text{BrO}_4\text{F}^-$ dissociation reactions and relative energies from two pure DFT methods, demonstrating that this system is a challenge for DFT methods.

Although the $\text{FBr-O}_2\text{-O}_2/(\text{FBr-O}_2\text{-O}_2)^-$ chain structures have been found to be the most stable isomers, yet there is no workable reaction mechanism for the formation of these species considering only BrF or BrF^- , BrO and O_2 or O_2^- as starting materials. According recently report on bromine (VII) BrO_3F_2^- anion [31], we conclude that the Br(VII) structure, $\text{FBrO}_3\text{...O}$ (**g**: C_{3v} , $^3\text{A}_1$) are the most likely structure for neutral BrO_4F , and the BrO_4F^- may have Br(V) (FO...BrO_3) $^-$ (**ac**: $^2\text{A}'$) complex structure. The DFT-based local reactivity descriptors such as the global or local softness or hardness, condensed Fukui functions can demonstrate this suggestion.

The DFT methods are able to describe the electronic structure of these systems with accuracies comparable to traditional correlated molecular orbital methods at a decreased computational cost. Furthermore these DFT-based local descriptors techniques are observed to assign more bonding character to the BrO_4F Lewis system.

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