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Electron Affinities of the Bromine Fluorides, BrF_n ($n = 1-7$)

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Abstract: The molecular structures, electron affinities, and dissociation energies of the BrF_n/BrF_n^- ($n = 1-7$) molecules have been examined using hybrid Hartree−Fock/density functional theory (DFT). The three different types of electron affinities reported in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The first Br−F dissociation energies of the BrF_n and BrF_n^- species have also been reported. The basis set used in this work is of double-ζ plus polarization quality with additional s- and p-type diffuse functions, and is denoted as DZP^{++}. Four different density functionals were used in this work. Among these, the best for predicting molecular structures and energies was found to be BHLYP, while other methods generally overestimated bond lengths. The most reliable adiabatic electron affinities, obtained at the DZP^{++} BHLYP level of theory, are 3.41 (Br), 2.64 (BrF), 4.78 (BrF_2), 3.77 (BrF_3), 5.58 (BrF_4), 4.24 (BrF_5), and 5.59 eV (BrF_6). The electron affinity of the Br atom predicted by this work is in good agreement with the experimental result, but not one of the molecular electron affinities (BrF_n, $n = 1-7$) is known. The neutral BrF_n bond distances range from 1.70 to 1.83 Å. However, the diatomic BrF^- distance and the axial Br−F distances in $BrF_3^-$and BrF_5^- are much longer, 2.25−2.30 Å, suggesting that the bonding in these three anions is quite different from that of their neutral counterparts.

I. Introduction

The BrF_n/BrF_n^- ($n = 1-7$) series of molecules, members of the interhalogen family, are all rather reactive. The bromine fluorides react vigorously with both organic and inorganic molecules. They are also very corrosive, oxidizing substances that have a tendency to attack most other elements and hydrolyze rapidly.[1,2] While stable in comparison to the radical members of this series, the explosive reactions of (closed shell) BrF_3 and BrF_5 have made studies of even these species difficult.[3,4] Despite their violent chemical properties, these molecules have been studied extensively in connection with atmospheric chemistry;[5,6] bromine-containing molecules that are released to the atmosphere, primarily by fire extinguishers, may play a role in the depletion of the ozone layer.[7] Nevertheless, there seem to be no experimental or theoretical data for the electron affinities (EAs), a fundamental property, of the bromine fluorides. The possibility that the bromine fluoride anions could play a significant role in atmospheric chemistry makes their electron affinities attractive research targets.

In predicting molecular energies and structures, there are many theoretical approaches, but considering both reliability and computational expense, gradient corrected density functional theory (DFT) has been shown to be effective for many related inorganic species such as the SF_n/SF_n^-, PF_n/PF_n^-, ClF_n/ClF_n^-, SiF_n/SiF_n^-, and $C_2F_n/C_2F_n^-$ molecules.[8−12] In addition, while the prediction of an electron affinity is generally difficult due to being the result of a small difference between two very large energies, these previous works have shown that DFT can be a dependable source for EA predictions. For a recent systematic study of DFT with regards to EA determinations, one is referred to the 1996 work of Galbraith and Schaefer.[8b] The main objective of this study, therefore, is to provide theoretical data for the electron affinities of the bromine fluorides.

II. Theoretical Methods

The four different density functional or hybrid Hartree−Fock/density functional forms used are Becke's 1988 exchange functional[13] with Lee, Yang, and Parr's correlation functional[14] (BLYP), Becke's half-and-half exchange functional[15] with the LYP correlation functional (BHLYP), Becke's three-parameter semiempirical exchange functional[16] with the LYP correlation functional (B3LYP), and Becke's 1988 exchange functional with the Perdew correlation functional[17] (BP86). A restricted Hartree−Fock (RHF) reference was used for all closed shell systems, while an unrestricted (UHF) wave function was employed for open-shell species. All the electron affinities and molecular structures have been determined with the Gaussian 94[18] (for BLYP, B3LYP, and BP86) and the Gaussian 92[19] (for BHLYP) program suites. The default integration grid of Gaussian 94 was also applied in the

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Table 1. Zero-Point Vibrational Energies within the Harmonic Approximation for the BrF_n/BrF_n^- ($n = 1-6$) at the DZP^{++} B3LYP Level of Theory in eV (kcal/mol in parentheses)

compd	ZPVE	compd	ZPVE	compd	ZPVE
BrF	0.041 (0.95)	BrF_3	0.160 (3.69)	BrF_5	0.312 (7.20)
BrF^-	0.016 (0.36)	BrF_3^-	0.104 (2.40)	BrF_5^-	0.215 (4.96)
BrF_2	0.074 (1.71)	BrF_4	0.207 (4.78)	BrF_6	0.338 (7.79)
BrF_2^-	0.077 (1.77)	BrF_4^-	0.177 (4.07)	BrF_6^-	0.284 (6.55)

Gaussian 92 work. The integrals that are evaluated in this study should be accurate to 1×10^{-5} E_h, the density was converged to 1×10^{-8} E_h, and Cartesian gradients were converged to at least 10^{-6} au.

The DZP^{++} basis set for bromine used herein was constructed with Ahlrichs' standard double-ζ *spd* set[20] with the addition of one set of *d*-like polarization functions [$\alpha_d(Br) = 0.389$][20] as well as a single set of diffuse *s* [$\alpha_s(Br) = 0.0469096$] and *p* [$\alpha_p(Br) = 0.0465342$] functions. The corresponding basis on fluorine was comprised of the standard Huzinage–Dunning–Hay[21] double-ζ *sp* set with one set of *d* polarization functions [$\alpha_d(F) = 1.000$] as well as a set of diffuse *s* [$\alpha_s(F) = 0.1049$] and *p* [$\alpha_p(F) = 0.0826$] functions. The diffuse function orbital exponents were determined in an "even tempered sense" as a mathematical extension of the primitive set, according to the formula of Lee and Schaefer.[22] Pure angular momentum *d* functions were used throughout. The final contraction scheme for this basis is Br (15s12p6d/9s7p3d) and F (10s6p1d/5s3p1d).

The geometries reported in Figures 1–6 were found to be energy minima after determining the harmonic vibrational frequencies at the corresponding stationary point structures with the DZP^{++} B3LYP level of theory. Zero-point vibrational energies (ZPVE) evaluated at this level are presented in Table 1. The ZPVE differences between BrF_n and BrF_n^- ($n = 1-6$) are quite small, in the range of 0.003 to 0.097 eV. These differences could be used as a correction to the adiabatic electron affinities.

The electron affinities are evaluated as a difference in total energies in the following manner: the adiabatic electron affinities are determined by,

$$EA_{ad} = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})}$$

the vertical electron affinities by,

$$EA_{vert} = E_{(\text{optimized neutral})} - E_{(\text{anion at neutral equilibrium geometry})}$$

and the vertical detachment energy by,

$$VDE = E_{(\text{neutral at anion equilibrium geometry})} - E_{(\text{optimized anion})}$$

The dissociation energies for BrF_n/BrF_n^- are determined by the difference in total energies in the following manner: the first dissociation energies for the neutrals refer to the reaction

$$BrF_n \rightarrow BrF_{n-1} + F \qquad (1)$$

while the first dissociation energy for the anions refers to the two different reactions,

$$BrF_n^- \rightarrow BrF_{n-1}^- + F \qquad (2)$$

$$BrF_n \rightarrow BrF_{n-1} + F^- \qquad (3)$$

III. Results and Discussion

A. Br and Br$^-$. The electron affinities of the $^2P_{3/2}$ state of the Br atom at various levels of theory, as well as experimental electron affinity data, are reported in Table 2. Values are determined from total energies of the Br atom and the Br^- ion. All four functionals predict the electron affinity of the Br atom to within 0.32 eV, and all values are larger than the experimental value of 3.36 eV given by Blondel, Cacciani, Delsart, and Trainham's laser-photodetachment threshold spectroscopy study of the Br anion.[23] The greatest correlation with experiment is achieved by DZP^{++} BHLYP, whose EA value is only 0.05 eV larger than experiment. The fact that BHLYP gives the best predictions for electron affinities was also noted in our earlier works on the second-row fluorides.[8–12] Since no experimental data are available for the BrF_n electron affinities, the comparison of the predicted EA at different levels of theory for the Br atom with experiment should be a dependable calibrator. In the following discussions for the BrF_n molecules, we will mainly use the DZP^{++} BHLYP results unless otherwise indicated.

B. BrF and BrF$^-$. Our optimized geometries for the ground $^1\Sigma^+$ state of BrF and the ground $^2\Sigma^+$ state of BrF^- are shown in Figure 1. All theoretical bond distances are longer than the experimental value for the neutral. The prediction closest to the experimental r_e of 1.759 Å obtained from Willis and Clark's microwave data[24a] for BrF came from the DZP^{++} BHLYP method, which gave a bond length of 1.756 Å. The bond lengths predicted by other functionals were overestimated by as much as 0.06 Å. Here we note the general trend for bond lengths yielded for the bromine fluorides as BLYP > BP86 > B3LYP > BHLYP. For the BrF^- ion, the DZP^{++} BHLYP bond length is 2.300 Å, longer by roughly 0.55 Å than that of the neutral species. We will discuss this large structural difference between neutral and anion later.

Table 3 contains the electron affinities for the adiabatic and vertical processes, as well as the vertical detachment energies for the BrF, BrF_2, BrF_3, BrF_4, BrF_5, and BrF_6 species. Note that the adiabatic values are not corrected for zero-point vibrational energy. Relying upon BHLYP, we report 2.64 eV as the most reliable adiabatic electron affinity for BrF based on our data for the EA of the Br atom and previous work[8,10] on the sulfur and chlorine fluorides. One may note that the values for EA_{ad}, EA_{vert}, and VDE are significantly different due to the large bond length difference between the neutral and the anion (vide infra). The range for EA_{vert} is from 1.06 to 1.45 eV and the range for VDE is from 4.24 to 4.48 eV. Furthermore, from the positive values for EA_{vert} and VDE, one may readily see that the anion is thermodynamically stable.

C. BrF$_2$ and BrF$_2^-$. The equilibrium geometries of the BrF_2 ground state ($^2A_1$) and the BrF_2^- ground state ($^1\Sigma_u^+$) are displayed in Figure 2. The BrF_2 radical has a bent structure

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Table 2. The Electron Affinities of Br in eV (kcal/mol in parentheses)[a]

method	EA
BHLYP	3.41 (78.7)
B3LYP	3.60 (83.1)
BP86	3.68 (85.0)
BLYP	3.46 (79.9)
exptl	3.36 (77.5)[b]

[a] All results obtained with DZP^{++} basis set. [b] Reference 23.

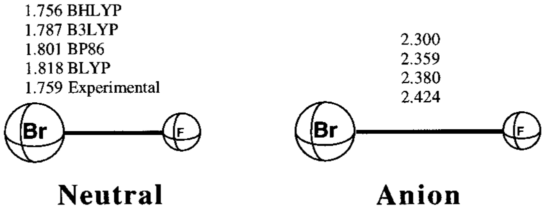

Figure 1. The molecular geometries of the X $^1\Sigma^+$ state of BrF and the X $^2\Sigma^+$ state of the anion, BrF^-. All bond lengths are in Å and all results were obtained with the DZP^{++} basis set.

Table 3. Adiabatic and Vertical Electron Affinities of the Neutral and Vertical Detachment Energies of the Anionic Bromine Monofluoride (BrF), Bromine Difluoride (BrF_2), Bromine Trifluoride (BrF_3), Bromine Tetrafluoride (BrF_4), Bromine Pentafluoride (BrF_5), and Bromine Hexafluoride (BrF_6) in eV (kcal/mol in parentheses)[a]

compd	method	EA_{ad}	EA_{vert}	VDE
BrF	BHLYP	2.64 (60.8)	1.06 (24.3)	4.48 (103.4)
	B3LYP	2.80 (64.7)	1.36 (31.3)	4.47 (103.1)
	BP86	2.79 (64.3)	1.45 (33.4)	4.34 (100.0)
	BLYP	2.71 (62.5)	1.36 (31.3)	4.24 (97.7)
BrF_2	BHLYP	4.78 (110.2)	3.83 (88.3)	6.28 (145.0)
	B3LYP	4.71 (108.6)	4.07 (93.8)	6.59 (151.9)
	BP86	4.47 (103.0)	4.11 (94.8)	4.73 (109.0)
	BLYP	4.34 (100.2)	4.00 (92.3)	4.60 (106.1)
BrF_3	BHLYP	3.77 (87.0)	1.78 (40.9)	5.96 (137.5)
	B3LYP	3.89 (89.7)	2.18 (50.4)	5.53 (127.6)
	BP86	3.74 (86.3)	2.27 (52.4)	5.05 (116.6)
	BLYP	3.76 (86.8)	2.30 (52.9)	5.03 (116.0)
BrF_4	BHLYP	5.58 (128.7)	4.23 (97.5)	6.61 (152.5)
	B3LYP	5.58 (128.6)	4.58 (105.7)	6.76 (155.9)
	BP86	5.25 (121.2)	4.64 (107.0)	5.54 (127.7)
	BLYP	5.21 (120.1)	4.66 (107.6)	5.47 (126.1)
BrF_5	BHLYP	4.24 (97.7)	1.68 (38.8)	6.99 (161.2)
	B3LYP	4.48 (103.3)	2.45 (56.5)	6.30 (145.4)
	BP86	4.32 (99.6)	2.66 (61.3)	5.65 (130.2)
	LYP	4.44 (102.5)	2.82 (65.0)	5.69 (131.2)
BrF_6	BHLYP	5.59 (129.0)	4.84 (111.6)	6.20 (142.9)
	B3LYP	6.10 (140.7)	5.48 (126.4)	6.61 (152.4)
	BP86	6.12 (141.1)	5.56 (128.1)	6.59 (151.9)
	BLYP	6.19 (142.7)	5.68 (130.9)	6.61 (152.5)

[a] Values are not corrected for ZPVE and were obtained with the DZP^{++} basis set.

with a bond angle of 154−169° as predicted by the four different functionals. The neutral Br−F bond length is in the range from 1.826 to 1.906 Å. As was the case for BrF, the DZP^{++} BHLYP method gives the shortest bond length for BrF_2. BrF_2^- is linear ($D_{\infty h}$), with Br−F bond distances predicted from 1.959 to 2.045 Å. These distances are only about 0.1 Å longer than their neutral counterparts, which is understandable as the BrF_2 radical's singly occupied molecular orbital (SOMO) is a π-type orbital, thus having little overall effect on the bond length (vide infra).

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 3. The predicted range of EA_{ad} is from 4.34 to 4.78 eV, among which the DZP^{++} BHLYP method predicts the largest value (4.78 eV). The range of EA_{vert} is from 3.83 to 4.11 eV and the range of VDE is from 4.60 to 6.59 eV. Note that because the difference in the geometries of the neutral and the anion are not as great as that for BrF, there are smaller energy gaps between EA_{ad}, EA_{vert}, and VDE.

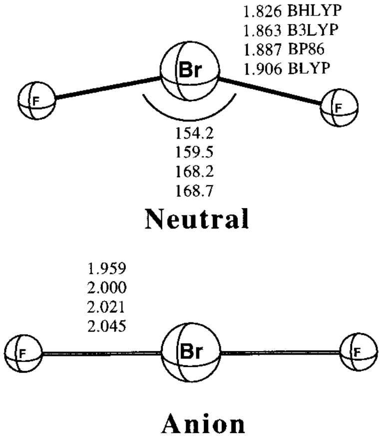

Figure 2. The molecular geometries of the X $^2A_1$ state of BrF_2 and the X $^1\Sigma_u^+$ state of the anion, BrF_2^-. Bond lengths and bond angles are in Å and deg, respectively. All results were obtained with the DZP^{++} basis set.

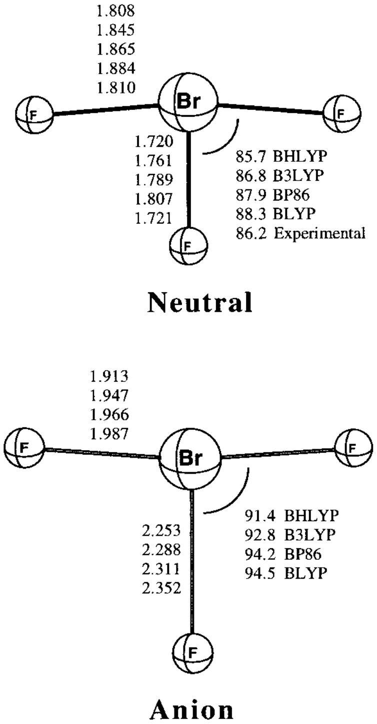

Figure 3. The molecular geometries of the X $^1A_1$ state of BrF_3 and the X $^2A_1$ state of the anion, BrF_3^-. Bond lengths and bond angles are in Å and deg, respectively. All results were obtained with the DZP^{++} basis set.

D. BrF_3 and BrF_3^-. The C_{2v} symmetry equilibrium geometries of the X $^1A_1$ state of BrF_3 and the X $^2A_1$ state of BrF_3^- are shown in Figure 3. The bond length predictions of the four functionals follow the same trends as above. Those predicted by the BHLYP method were again the closest to the experimental values. The gas-phase structure of BrF_3 was reported by Magnuson as 1.810 and 1.721 Å for the Br−F_{eq} and Br−F_{ax} bond distances and 86.2° for the F−Br−F bond angle, respectively,[25] while the DZP^{++} BHLYP method predicts them as 1.808 Å, 1.720 Å, and 85.7°. All four theoretical

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Table 4. Dissociation Energies (D_{BrFn}) for the Neutral Members of the Series in eV (kcal/mol in parentheses)[a]

dissociation	BHLYP	B3LYP	BP86	BLYP	exptl
$BrF \rightarrow Br + F$	1.93 (44.5)	2.54 (58.6)	2.97 (68.6)	2.87 (66.1)	2.55 (58.8)[b] 2.38 (54.9)[c]
$BrF_2 \rightarrow BrF + F$	0.64 (14.7)	1.40 (32.2)	2.02 (46.6)	1.96 (45.2)	
$BrF_3 \rightarrow BrF_2 + F$	1.67 (38.5)	2.10 (48.4)	2.44 (56.3)	2.29 (52.8)	
$BrF_4 \rightarrow BrF_3 + F$	0.40 (9.3)	1.18 (27.1)	1.85 (42.7)	1.77 (40.8)	
$BrF_5 \rightarrow BrF_4 + F$	1.70 (39.2)	2.03 (46.8)	2.34 (54.0)	2.13 (49.0)	
$BrF_6 \rightarrow BrF_5 + F$	−0.02 (−0.4)	0.69 (16.0)	1.19 (27.4)	1.07 (24.6)	

[a] Values are not corrected for ZPVE and were obtained with the DZP^{++} basis set. [b] Reference 24. [b] Reference 33.

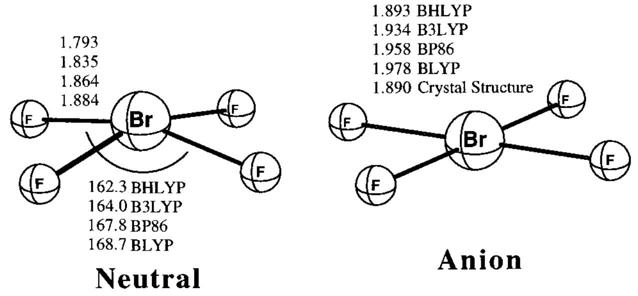

Figure 4. The molecular geometries of the X $^2A_1$ state of BrF_4 and the X $^1A_1$ state of the anion, BrF_4^-. Bond lengths and bond angles are in Å and deg, respectively. All results were obtained with the DZP^{++} basis set.

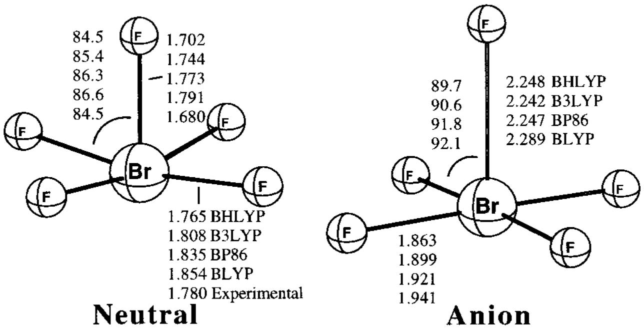

Figure 5. The molecular geometries of the X $^1A_1$ state of BrF_5 and the X $^2A_1$ state of the anion, BrF_5^-. Bond lengths and bond angles are in Å and deg, respectively. All results were obtained with the DZP^{++} basis set.

methods do a reasonable job in predicting the important difference between the equatorial and axial Br−F bond distances. Our BrF_3 structure is also in qualitative agreement with an earlier theoretical study that employed the MP2/6-311+G* method and took into account the effects of relativity.[26]

For the BrF_3^- ion, there are no experimental data with which to compare. The trend for the theoretical bond lengths is similar. The DZP^{++} BHLYP method predicts the geometrical parameters as 1.913 Å, 2.253 Å, and 91.4° for $Br-F_{eq}$, $Br-F_{ax}$, and ∠FBrF, respectively. Note that the $Br-F_{ax}$ bond distance is nearly 0.5 Å longer than that of neutral BrF_3. Clearly the bonding in the radical anion, BrF_3^-, is quite different from that of the neutral. The reason for this will become clear in our discussion of the BrF_5 species below.

The most reliable adiabatic electron affinity is 3.77 eV from BHLYP. The substantial value of this EA is perhaps surprising given the fact that BrF_3 is a relatively stable molecule, at least as far as bromine fluorides go. In previous work on the sulfur[8] analogues, for which many experimental EA values exist, it was found that DFT may slightly overestimate (<0.6 eV) the electron affinities of the larger species (SF_n; $n = 5, 6$); however the DZP^{++} BHLYP method provided excellent agreement for the $n = 1-4$ series and was usually within 0.2 eV of experiment. Therefore, the large EA_{ad} value for BrF_3 should be regarded as a dependable target for this molecule. The EA_{ad} values obtained for BrF_3 from the other functionals are in good agreement with BHLYP, showing deviations of about (or less than) 0.1 eV. The EA_{vert} range is from 1.78 to 2.30 eV, and the range for VDE is from 5.03 to 5.96 eV. Again, these large differences between EA_{ad}, EA_{vert}, and VDE are due to the large difference in geometry between BrF_3 and BrF_3^-.

E. BrF_4 and BrF_4^-. The optimized C_{4v} geometry of the X $^2A_1$ state of BrF_4 and the D_{4h} symmetry structure of the X $^1A_1$ state of BrF_4^- are shown in Figure 4. DZP^{++} BHLYP predicts, an r_e of 1.793 and 1.893 Å for the neutral and anion, respectively. The only experimental structure data for the anion is provided by an X-ray crystal structure of $KBrF_4$.[27] The bond length according to this study was 1.890 Å, which differs by 0.03 Å from the DZP^{++} BHLYP result. However, as the BrF_4 anion was studied as an ionic complex with the potassium cation, this comparison may not be entirely valid; the agreement, though, between the gas-phase equilibrium geometry and the crystal structure is certainly satisfactory. The bond lengths provided by the other DFT functionals were longer by as much as 0.09 Å.

Our predicted adiabatic electron affinity for BrF_4 is 5.58 eV. The EA_{vert} ranges from 4.23 to 4.66 eV and the VDE ranges from 5.47 to 6.76 eV. Again, this is a very large electron affinity, strongly suggesting the observability of BrF_4^- in a carefully designed experiment. Like BrF_2, the EA_{ad}, EA_{vert}, and VDE values are similar due to the small difference in geometry between neutral and anion.

F. BrF_5 and BrF_5^-. The C_{4v} equilibrium geometry of the X $^1A_1$ state of the BrF_5 and the C_{4v} geometry of the X $^2A_1$ state of BrF_5^- are shown in Figure 5. Once again, the DZP^{++} BHLYP method provides an equilibrium structure in good agreement with experiment, yielding values of 1.680 Å, 1.785 Å, and 83.5° for r_{ax}, r_{eq}, and $\angle F_{ax}-Br-F_{eq}$, respectively. X-ray crystal data, reported by Burbank and Bensey in 1957, yielded the first look at this reactive species and gave an r_{ax} of 1.680 Å and an r_{eq} of 1.780 Å.[28] They also reported a slightly acute $F_{ax}-Br-F_{eq}$ angle of 84.5°. More recent data[29] on the structure of this species are available; however, little has changed in the more than 40 years since Burbank and Bensey's study. Combining electron diffraction and microwave data in 1971, Robliette, Bradley, and Brier[29a] provided a gas-phase structure for BrF_5, obtaining r_α values of 1.69 and 1.77 Å for $Br-F_{ax}$ and $Br-F_{eq}$, respectively. The $F_{ax}-Br-F_{eq}$ angle was given as 84.8°. Similar to both BrF^- and BrF_3^-, the BrF_5^- ion has longer Br−F bond distances than the neutral, especially for $Br-F_{ax}$,

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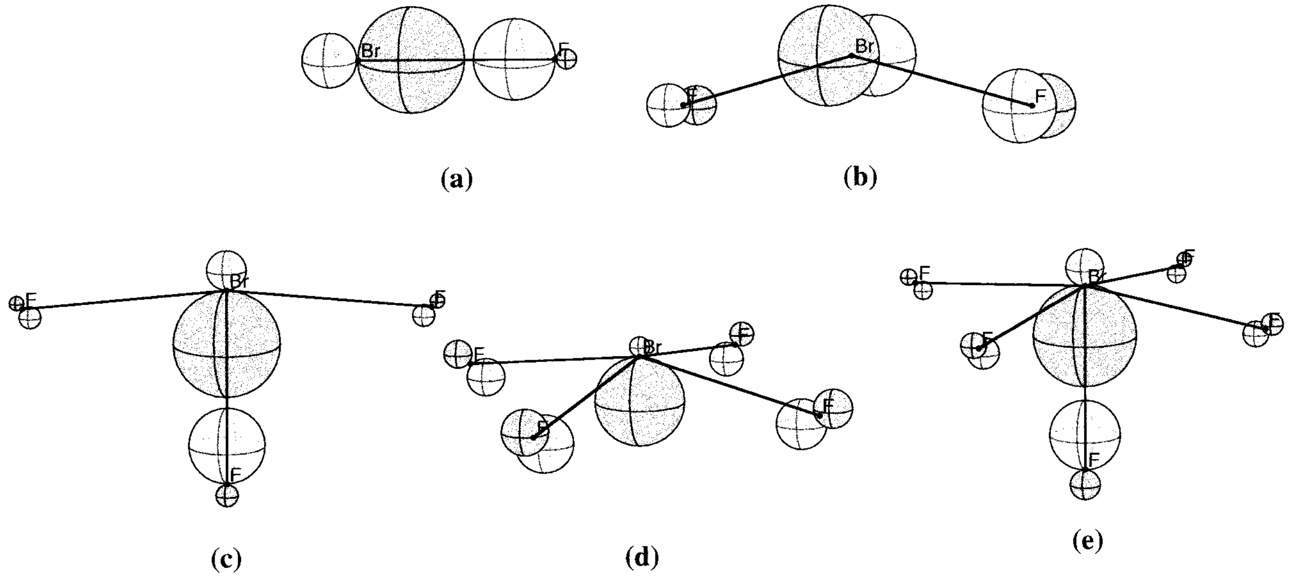

Figure 6. The lowest unoccupied (BrF, BrF$_3$, and BrF$_5$) and singly occupied (BrF$_2$ and BrF$_4$) molecular orbitals: (a) 11σ, LUMO of BrF; (b) 5b_1, SOMO of BrF$_2$; (c) 16a_1, LUMO of BrF$_3$; (d) 12a_1, SOMO of BrF$_4$; and (e) 15a_1, LUMO of BrF$_5$.

which increases by about 0.5 Å. Again, as with BrF$^-$ and BrF$_3^-$ it is clear that the bonding in the anion (BrF$_5^-$) must be quite different from that for the closed-shell neutral species.

In Figure 6 we show the lowest unoccupied (BrF, BrF$_3$, and BrF$_5$) and singly occupied (BrF$_2$ and BrF$_4$) molecular orbitals. From these orbital plots, it is relatively easy to determine why the bond length differences between neutral and anionic bromine fluorides which contain an odd number of F atoms are so much greater than the corresponding differences in those bromine fluorides with even numbers of F atoms. Notice that the LUMO of BrF has a substantial amount of antibonding σ character. Adding electron density to this orbital should lower the bond order and substantially increase the Br−F bond length. This is also true in BrF$_3$ and BrF$_5$, in which the LUMOs again have substantial antibonding character along the axial Br−F bonds. The radicals, BrF$_2$ and BrF$_4$, do not suffer from this problem, as the anion can be formed by adding the additional electron in the π-type SOMOs, which have little effect on the actual bond length. These orbitals do, on the other hand, have rather dramatic effects on the overall symmetry of these species. Notice that in neutral BrF$_4$, the 12a_1 orbital largely favors a square-planar geometry, and an additional electron in this orbital is going to force BrF$_4^-$ to adopt this structure.

The adiabatic and vertical electron affinities and vertical detachment energies are reported in Table 3. The most reliable prediction of the adiabatic electron affinity of BrF$_5$ is 4.24 eV. The large magnitude of this EA suggests that BrF$_5^-$ should be observable and could play a role in atmospheric chemistry. Even though it has been suggested that with these larger species (BrF$_n$; n = 5,6) DFT may overestimate EAs, the largest error observed for the SF$_6$ species was 0.56 eV.[8] The range 4.2−4.5 eV, then, engulfs our predicted EA$_{\text{ad}}$ for BrF$_5$. The EA$_{\text{vert}}$ values range from 1.68 to 2.82 eV and the range for VDE is from 5.65 to 6.99 eV.

G. BrF$_6$ and BrF$_6^-$. The equilibrium octahedral (O_h) structures of the X ^{2}A$_{1g}$ state of BrF$_6$ and the O_h structure of the X ^{1}A$_{1g}$ state of BrF$_6^-$ are shown in Figure 7. Since there are no experimental data for these species, the most reliable Br−F bond distances are believed to be the BHLYP results, 1.773 Å for the neutral and 1.865 Å for the anion. For comparison with other theoretical work done on the BrF$_6^-$ ion, the bond length obtained by MP2 theory conjoined with a basis set of triple-ζ plus polarization quality (referred to as TZVP) was 1.910 Å,[30] which is 0.045 Å larger than our DZP^{++} BHLYP (1.865 Å) result. This difference between theoretical methods is understandable due to the widely known fact that second-order perturbation theory almost always provides equilibrium bond lengths which are too long, even in the complete basis set limit.[31] The most reliable single prediction of the adiabatic electron affinity of BrF$_6$ is 5.59 eV, while the EA$_{\text{vert}}$ range is from 4.84 to 5.68 eV and the range for the VDE is from 6.20 to 6.61 eV.

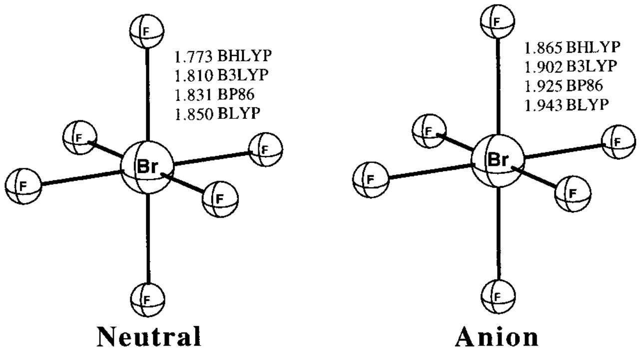

Figure 7. The molecular geometries of the X ^{2}A$_{1g}$ state of BrF$_6$ and the X ^{1}A$_{1g}$ state of the anion, BrF$_6^-$. Bond lengths and bond angles are in Å and deg, respectively. All results were obtained with the DZP^{++} basis set.

H. BrF$_7$ and BrF$_7^-$. Since iodine heptafluoride is known to exist, we have investigated the D_{5h} structures of BrF$_7$ and BrF$_7^-$. The stationary points from the DZP^{++} BHLYP method have bond distances Br−F$_{\text{ax}}$ = 1.689 Å and Br−F$_{\text{eq}}$ = 1.793 Å for the neutral BrF$_7$ molecule and Br−F$_{\text{ax}}$ = 1.789 Å and Br−F$_{\text{eq}}$ = 1.890 Å for the BrF$_7^-$ ion. The energy difference between them is 6.21 eV. However, neither of the D_{5h} structures are genuine minima, so this energy difference cannot be regarded as a true electron affinity. Due to the extreme multivalent nature of this species, perhaps the addition of f-like polarization functions would be important in locating the minima for both the neutral and its anion.

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Table 5. Dissociation Energies (D_{BrFn^-}) for the Anionic Members of the Series in eV (kcal/mol in parentheses)

dissociation	BHLYP	B3LYP	BP86	BLYP
$BrF^- \rightarrow Br^- + F$	1.15 (26.6)	1.74 (40.2)	2.08 (47.9)	2.12 (48.8)
$BrF_2^- \rightarrow BrF^- + F$	2.78 (64.1)	3.30 (76.1)	3.70 (85.3)	3.59 (82.8)
$BrF_3^- \rightarrow BrF_2^- + F$	0.66 (15.3)	1.28 (29.5)	1.72 (39.6)	1.71 (39.4)
$BrF_4^- \rightarrow BrF_3^- + F$	2.21 (51.0)	2.87 (66.1)	3.36 (77.5)	3.21 (74.0)
$BrF_5^- \rightarrow BrF_4^- + F$	0.35 (8.1)	0.93 (21.4)	1.41 (32.5)	1.36 (31.4)
$BrF_6^- \rightarrow BrF_5^- + F$	1.34 (30.9)	2.31 (53.4)	2.99 (68.8)	2.81 (64.8)
$BrF^- \rightarrow Br + F^-$	1.63 (37.5)	1.80 (41.5)	2.13 (49.0)	1.78 (41.0)
$BrF_2^- \rightarrow BrF + F^-$	2.47 (57.1)	2.56 (59.1)	2.85 (65.7)	2.50 (57.6)
$BrF_3^- \rightarrow BrF_2 + F^-$	2.50 (57.7)	2.45 (56.4)	2.55 (58.8)	2.25 (51.9)
$BrF_4^- \rightarrow BrF_3 + F^-$	3.04 (70.1)	3.21 (74.0)	3.47 (80.0)	3.17 (73.2)
$BrF_5^- \rightarrow BrF_4 + F^-$	2.99 (69.0)	2.96 (68.3)	3.03 (69.8)	2.77 (63.8)
$BrF_6^- \rightarrow BrF_5 + F^-$	2.63 (60.7)	3.25 (74.9)	3.67 (84.6)	3.45 (79.6)

[a] Values are not corrected for ZPVE and were obtained with the DZP^{++} basis set.

I. Dissociation Energies. The neutral and anionic bond dissociation energies for BrF_n/BrF_n^- ($n = 1-6$) are given in Tables 4 and 5. The DZP^{++} BHLYP dissociation energies are much lower than those from the other three methods. It was found in the previous studies of SF_n and ClF_n[8,11] that the DZP^{++} BHLYP predictions for dissociation energies were clearly the worst of the four functionals employed. As the DFT/HF hybrid BHLYP functional purports to include standard Hartree–Fock theory to the greatest degree of all the functionals used in this study, this finding is not surprising. It is well-known that Hartree–Fock theory (without the inclusion of dynamical or nondynamical correlation) performs dismally for bond-breaking processes.[32]

Table 4 shows the dissociation energies (for the process $BrF_n \rightarrow BrF_{n-1} + F$) of the neutral molecules. Excluding the DZP^{++} BHLYP results, the dissociation energy for BrF ranges from 2.54 to 2.97 eV. There is more than one experimental value for the dissociation energy of BrF. In the 1968 edition of his authoritative book on diatomic dissociation energies, Gaydon recommends $D_0(BrF) = 2.384$ eV (55.0 kcal/mol).[33] Huber and Herzberg, in their comprehensive 1979 book on diatomic molecules, recommend $D_0(BrF) = 2.548$ eV (58.76 kcal/mol).[24b] And from the heat of formation (0 K) as −50.8, 117.917, and 77.284 kJ/mol for BrF, Br, and F, respectively, in the 1985 JANAF tables,[34] the dissociation energy can be derived as 2.552 eV (58.9 kcal/mol). Best agreement with any of the experimental dissociation energies is provided by the B3LYP method.

The theoretical dissociation energies for BrF_2 decrease to the range of between 1.40 and 1.96 eV. The data of Table 4 show that this value increases for BrF_3 and decreases for BrF_4 again. The same trend continues for BrF_5 and BrF_6. In other words, the dissociation energies become larger for BrF_n when n is an odd number, and smaller when n is an even number. This zigzag phenomenon can be readily explained. The BrF_n molecules with even number n are radicals, and are less stable than those with odd n, which have closed shell electronic structures. Another trend is that when the odd number n increases (i.e. from 1, to 3, to 5), the dissociation energy decreases. The molecules with even numbers follow the same trend. This indicates in a qualitative way that the larger BrF_n molecules are less stable than the smaller ones, which is understandable due to their increased hypervalency.

For the anions, BrF_n^-, there are two forms of dissociation: either to a neutral BrF_{n-1} plus an F^- ion, or to a BrF_{n-1}^- ion plus a neutral F atom. Excluding the DZP^{++} BHLYP dissociation energies, which are significantly smaller than the others, Table 5 shows that, for the dissociation to "$BrF_{n-1}^- + F$", the zigzag phenomenon is similar to that in Table 4. The amplitude of the zigzag is significant and the general trend is downward. The difference is that the molecules with even number n are more stable since they have closed shell electronic structures. This may also be related to the fact that when n is odd, the additional electron of the anions is residing in an antibonding orbital (primarily a σ^* orbital), lengthening and destabilizing those σ bonds. However, for the dissociation to "$BrF_{n-1} + F^-$", the zigzag feature is not as obvious, and the general trend is upward. This indicates that when the size of the molecule increases, dissociation to a BrF_{n-1}^- ion plus a neutral F atom becomes preferable.

IV. Conclusions

On the basis of the experimental adiabatic electron affinity for the Br (3.36 eV) atom, and previous work on the SF_n/SF_n^-, PF_n/PF_n^- ClF_n/ClF_n^-, SiF_n/SiF_n^-, and $C_2F_n/C_2F_n^-$ molecules,[8−12] we have concluded that the DZP^{++} BHLYP method is the most reliable method for predicting the electron affinities [3.41 (Br), 2.64 (BrF), 4.78 (BrF_2), 3.78 (BrF_3), 5.58 (BrF_4), 4.24 (BrF_5), 5.59 eV (BrF_6)] and molecular structures of the bromine fluorides.

In predicting those structures for which experimental results were available (BrF, BrF_3, and BrF_5), the DZP^{++} BHLYP results were in closest agreement with the experimental structures, giving average bond distance errors for the four density functionals, BHLYP (0.009 Å), B3LYP (0.039 Å), BP86 (0.063 Å), and BLYP (0.081 Å).

Unlike predicting geometries and EAs for these molecules, the DZP^{++} BHLYP method is considered to yield the least reliable predictions of dissociation energies, as shown earlier for related molecules.[8−12] This may be correlated with the fact that the BHLYP functional incorporates the largest fraction of the ab initio Hartree–Fock method; thus similar to SCF, its performance for dissociation energies is less than desirable. The dissociation energy ranges for the neutral members of these interhalogens, excluding the DZP^{++} BHLYP values, are 2.54–2.97 (BrF), 1.40–2.02 (BrF_2), 2.10–2.44 (BrF_3), 1.18–1.85 (BrF_4), 2.03–2.34 (BrF_5), and 0.69–1.19 eV (BrF_6). Compared to the experimental dissociation energy for BrF (2.55 eV),[24b] our predictions are reasonable. The general trend in dissociation energy values is as follows: BP86 $\sim$ BLYP $>$ B3LYP $\gg$ BHLYP. The dissociation energy ranges for losing F from the BrF_n^- ions are 1.74–2.12 (BrF^-), 3.30–3.70 (BrF_2^-), 1.28–1.72 (BrF_3^-), 2.87–3.36 (BrF_4^-), 0.93–1.41 eV ($BrF_5{}^-$), and 2.31–2.99 eV (BrF_6^-). The general trend in dissociation energy values for BrF_2^-, BrF_4^-, and BrF_6^- is BP86 $>$ BLYP $>$ B3LYP $\gg$ BHLYP, and that for BrF^-, BrF_3^-, and BrF_5^- is BP86 $=$ BLYP $>$ B3LYP $\gg$ BHLYP. The dissociation energy ranges for losing F^- from the anion member of these molecules are 1.78–2.13 (BrF^-), 2.50–2.85 (BrF_2^-), 2.25–2.55 (BrF_3^-), 3.17–3.47 (BrF_4^-), 2.77–3.03 (BrF_5^-), and 3.25–3.67 eV (BrF_6^-), and the general trend of dissociation energy values for BrF_2^-, and BrF_4^- and BrF_6^- is BP86 $>$B3LYP $>$ BPYP $\sim$ BHLYP, and that for BrF_3^- and BrF_5^- is BP86 $>$ BHLYP $>$ B3LYP $>$ BLYP.

The range of bromine–fluorine bond distances predicted here is of special interest. For this purpose we consider only the BHLYP predictions. The neutral Br–F bond distances are 1.756

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(BrF), 1.826 (BrF_2), 1.720 and 1.808 (BrF_3), 1.793 (BrF_4), and 1.702 and 1.765 (BrF_5), 1.773 Å (BrF_6). Thus the entire range, from 1.702 to 1.826, is 0.124 Å. For the anions, we predict a much broader range of bromine−fluorine bond distances. The negative ion Br−F bond distances are 2.300 (BrF^-), 1.959 (BrF_2^-), 1.913 and 2.253 (BrF_3^-), 1.893 (BrF_4^-), 1.863 and 2.248 (BrF_5^-), and 1.865 Å (BrF_6^-). We see that the closed shell species BrF_2^- and BrF_4^- have Br−F bond distances similar to the neutral bromine fluorides. However, the distance for diatomic BrF^- and the axial distances in BrF_3^- and BrF_5^- are all much longer than those observed for the neutral bromine fluorides.

One is tempted via ideas such as Badger's rule to suggest that unusually long bond distances might be associated with low electron affinities. Such an argument may be applied to the BrF system, which has by far the smallest EA of the bromine fluorides, and also a very long anion bond distance. However, the longest Br−F distance of all is that predicted for the axial BrF_5^- distance, while the BrF_5 species has a very large EA, namely 4.24 eV. This phenomenon is not readily explainable. Additionally, due to the existence of IF_7, it is desirable to locate the corresponding bromine analogue. Future theoretical work involving larger basis sets with the added directionality provided by *f* and perhaps even *g* functions is recommended. We hope that our theoretical predictions can provide inspiration for the further experimental study of these important interhalogen compounds and their anions.

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