

## Hypervalency Avoided: Simple Substituted BrF<sub>3</sub> and BrF<sub>5</sub> Molecules. Structures, Thermochemistry, and Electron Affinities of the Bromine Hydrogen Fluorides HBrF<sub>2</sub> and HBrF<sub>4</sub>

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**Abstract:** Five different pure density functional theory (DFT) and hybrid Hartree–Fock/DFT methods have been used to search for the molecular structures, thermochemistry, and electron affinities of the bromine hydrogen fluorides HBrF<sub>n</sub>/HBrF<sub>n</sub><sup>−</sup> (*n* = 2, 4). The basis sets used in this work are of double- $\zeta$  plus polarization quality in conjunction with *s*- and *p*-type diffuse functions, labeled as DZP<sup>++</sup>. Structures with Br–F and Br–H normal bonds, that is, HBrF<sub>2</sub>/HBrF<sub>2</sub><sup>−</sup> with C<sub>2v</sub> or C<sub>s</sub> symmetry and HBrF<sub>4</sub>/HBrF<sub>4</sub><sup>−</sup> with C<sub>4v</sub> or C<sub>s</sub> symmetry, are genuine minima. However, unlike the original BrF<sub>3</sub> and BrF<sub>5</sub> molecules, the global minima for HBrF<sub>n</sub>/HBrF<sub>n</sub><sup>−</sup> (*n* = 2, 4) species are predicted to be complexes, some of which contain hydrogen bonds. The demise of the hypervalent structures is due to the availability of favorable dissociation products involving HF, which has a much larger dissociation energy than F<sub>2</sub>. Similar reasoning suggests that PF<sub>4</sub>H, SF<sub>3</sub>H, SF<sub>5</sub>H, ClF<sub>2</sub>H, ClF<sub>4</sub>H, AsF<sub>4</sub>H, SeF<sub>3</sub>H, and SeF<sub>5</sub>H will all be hydrogen bond structures incorporating diatomic HF. The most reasonable theoretical values of the adiabatic electron affinities (EA<sub>ad</sub>) are 3.69 (HBrF<sub>2</sub>) and 4.38 eV (HBrF<sub>4</sub>) with the B3LYP method. These electron affinities are comparable to those of the analogous molecules: Br<sub>2</sub>F<sub>n</sub>, ClBrF<sub>n</sub>, and BrF<sub>n+1</sub> systems. The first F-atom dissociation energies for the neutral global minima are 60 (HBrF<sub>2</sub>) and 49 kcal/mol (HBrF<sub>4</sub>) with the B3LYP method. The first H-atom dissociation energies for the same systems are 109 (HBrF<sub>2</sub>) and 116 kcal/mol (HBrF<sub>4</sub>). The large Br–H bond energies are not sufficient to render the hypervalent structures energetically tenable. The dissociation energies for the complexes to their fragments are relatively small.

### Introduction

The interhalogen compounds play a key role in organic synthesis and stratosphere chemistry.<sup>1–5</sup> Thus, theoretical interest in the interhalogens comes as no surprise. The diatomics BrF, BrCl, and BrI have been studied with many body perturbation theory methods (to the 4th order) by Kucharski et al.<sup>6</sup> and by Sadlej.<sup>7</sup> However, the previous studies of these molecules have been devoted mainly to the binary compounds, partly because the highly reliable convergent quantum mechanical methods are difficult to apply to larger molecules with current computational resources. The development of methods based on density functional theory (DFT) in recent years has allowed DFT methods to be applied to larger interhalogen molecules, for

example, ClBrF<sub>n</sub> and BrF<sub>n</sub>.<sup>8,9</sup> In a recent comprehensive review Rienstra-Kiracofe et al.<sup>10</sup> showed that several DFT methods appear to give reliable predictions of the structures and energetics of such systems. Because the stable closed-shell BrF, BrF<sub>3</sub>, and BrF<sub>5</sub> species have been prepared and thoroughly studied,<sup>11–13</sup> their mono-hydrogen substituted species are natural candidates for stability and playing a related role in chemistry. In addition to the well-known hydrobromic acid HBr, it is of interest to explore the potentially hypervalent compounds HBrF<sub>2</sub> and HBrF<sub>4</sub>. To our knowledge, no previous studies for these ternary hydrogen and halogen compounds have been reported.

In the present study, we consider the hydrogen bromine fluorides HBrF<sub>2</sub> and HBrF<sub>4</sub> and their anions with five selected DFT methods and investigate their properties, including geometries of different isomers, dissociation energies, and electron affinities (EA).

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## Theoretical Methods

Five different DFT or hybrid Hatree-Fock/DFT methods were used in this study: (1) BHandLYP, which is Becke's half and half HF/DFT hybrid exchange functional (BH)<sup>14</sup> combined with the Lee, Yang, and Parr correlation functional (LYP);<sup>15</sup> (2) B3P86, Becke's three-parameter functional<sup>16</sup>(B3) plus Perdew's correlation functional<sup>17</sup> (P86); (3) B3LYP, B3 combined with LYP; (4) BP86, incorporation of the Becke's 1988 exchange functional (B)<sup>18</sup> with P86; and (5) BLYP, which employs B along with LYP.

As in previous DFT studies,<sup>8,9,19</sup> standard double- $\zeta$  plus polarization basis sets were used, augmented with *s* and *p* diffuse functions, denoted DZP++. The basis set for bromine was composed of Ahlrichs' standard double- $\zeta$ <sup>20</sup> plus a set of *d*-type polarization functions [ $\alpha_d(\text{Br}) = 0.389$ ]<sup>20</sup> and adding diffuse functions [ $\alpha_s(\text{Br}) = 0.0469$ ] and [ $\alpha_p(\text{Br}) = 0.0465$ ]. The DZP++ basis sets for fluorine and hydrogen in this paper were composed of the standard Huzinaga–Dunning<sup>21,22</sup> double- $\zeta$  sets plus polarization functions [ $\alpha_d(\text{F}) = 1.00$ ,  $\alpha_p(\text{H}) = 0.75$ ], augmented with one set of diffuse functions [ $\alpha_s(\text{F}) = 0.1049$ ,  $\alpha_p(\text{F}) = 0.0826$ , and  $\alpha_s(\text{H}) = 0.04415$ ]. The final contracted basis is designated Br(15s12p6d/9s7p3d), F(10s6p1d/5s3p1d), and H(5s1p/3s1p). All computations were carried out using the Gaussian 98 program suite<sup>23</sup> in Beijing. The fine integration grid (99 590) was applied.

The geometries were optimized independently with each of the five DFT methods. Vibrational frequency analyses were carried out at each level, to assess the nature of the stationary points and to obtain zero point vibrational energies (ZPVE). It is found that the ZPVE corrections for EA<sub>ad</sub> are quite small (Table 1). The vibrational frequencies and infrared intensities for the different global minima are reported as Supporting Information.

Three forms of the neutral–anion energy separations are determined as differences in total energies: The adiabatic electron affinities are determined by

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

the vertical electron affinities by

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

and the vertical detachment energies (VDEs) by

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

The dissociation energies for these systems have also been predicted.

## Results and Discussions

**1. HBrF<sub>2</sub>/HBrF<sub>2</sub><sup>-</sup>.** The optimized equilibrium geometries for HBrF<sub>2</sub> are shown in Figure 1 (**2na**–**2ng**). Their relative energies

**Table 1.** ZPVEs within the Harmonic Approximation for the HBrF<sub>2</sub>/HBrF<sub>2</sub><sup>-</sup> and HBrF<sub>4</sub>/HBrF<sub>4</sub><sup>-</sup> Systems with DZP++ DFT Methods, in kcal/mol

compound	BHLYP	B3P86	B3LYP	BP86	BLYP
<b>2na</b> ( <sup>1</sup> A', C <sub>s</sub> )	7.88	7.71	7.55	7.44	7.29
<b>2nb</b> ( <sup>1</sup> A', C <sub>s</sub> )	8.44	8.14	8.05	7.79	7.72
<b>2nc</b> ( <sup>1</sup> Σ <sup>+</sup> , C <sub>∞v</sub> )	7.44	7.17	7.07	6.85	6.76
<b>2nd</b> ( <sup>1</sup> Σ <sup>+</sup> , C <sub>∞v</sub> )	8.00	7.57	7.52	7.14	7.11
<b>2ne</b> ( <sup>1</sup> A', C <sub>s</sub> )	<i>a</i>	7.65	7.50	7.37	7.25
<b>2nf</b> ( <sup>1</sup> A <sub>1</sub> , C <sub>2v</sub> )	7.81	7.41	7.29	6.96	6.83
<b>2ng</b> ( <sup>1</sup> A', C <sub>s</sub> )	7.97	7.53	7.37	7.00	6.84
<b>2aa</b> ( <sup>2</sup> A', C <sub>s</sub> )	8.20	7.93	7.83	7.53	7.44
<b>2ab</b> ( <sup>2</sup> Σ <sup>+</sup> , C <sub>∞v</sub> )	7.94	7.54	7.45	6.98	6.91
<b>2ac</b> ( <sup>2</sup> A', C <sub>s</sub> )	7.96	7.59	7.53	7.18	7.13
<b>2ad</b> ( <sup>2</sup> Σ <sup>+</sup> , C <sub>∞v</sub> )	7.60	7.22	7.16	6.77	6.72
<b>2ae</b> ( <sup>2</sup> B <sub>2</sub> , C <sub>2v</sub> )	5.45	4.98	4.87	4.65	4.52
<b>2af</b> ( <sup>2</sup> A <sub>1</sub> , C <sub>2v</sub> )	2.40	2.66	2.53	2.65	2.50
<b>4na</b> ( <sup>1</sup> A', C <sub>s</sub> )	11.71	11.30	11.05	10.74	10.50
<b>4nb</b> ( <sup>1</sup> A, C <sub>1</sub> )	11.75	11.26	11.06	10.61	10.40
<b>4nc</b> ( <sup>1</sup> A', C <sub>s</sub> )	10.75	10.22	10.08	10.01	9.84
<b>4nd</b> ( <sup>1</sup> A', C <sub>s</sub> )	10.25	10.00	9.80	10.05	9.81
<b>4ne</b> ( <sup>1</sup> A <sub>1</sub> , C <sub>4v</sub> )	12.42	11.63	11.40	10.73	10.49
<b>4nf</b> ( <sup>1</sup> A', C <sub>s</sub> )	12.23	11.39	11.13	10.41	10.14
<b>4aa</b> ( <sup>2</sup> A', C <sub>s</sub> )	10.80	10.31	10.15	9.66	9.53
<b>4ab</b> ( <sup>1</sup> A, C <sub>1</sub> )	10.62	10.30	10.14	9.78	9.64
<b>4ac</b> ( <sup>2</sup> A', C <sub>s</sub> )	<i>b</i>	9.78	9.58	9.29	9.12
<b>4ad</b> ( <sup>1</sup> A, C <sub>1</sub> )	10.29	10.09	9.95	9.51	9.38
<b>4ae</b> ( <sup>2</sup> A', C <sub>s</sub> )	10.29	9.99	9.85	9.37	9.24
<b>4af</b> ( <sup>2</sup> A', C <sub>s</sub> )	9.39	8.93	8.72	8.06	<i>c</i>

<sup>a</sup> Structure **2ne** is not a stationary point with the BHLYP method.

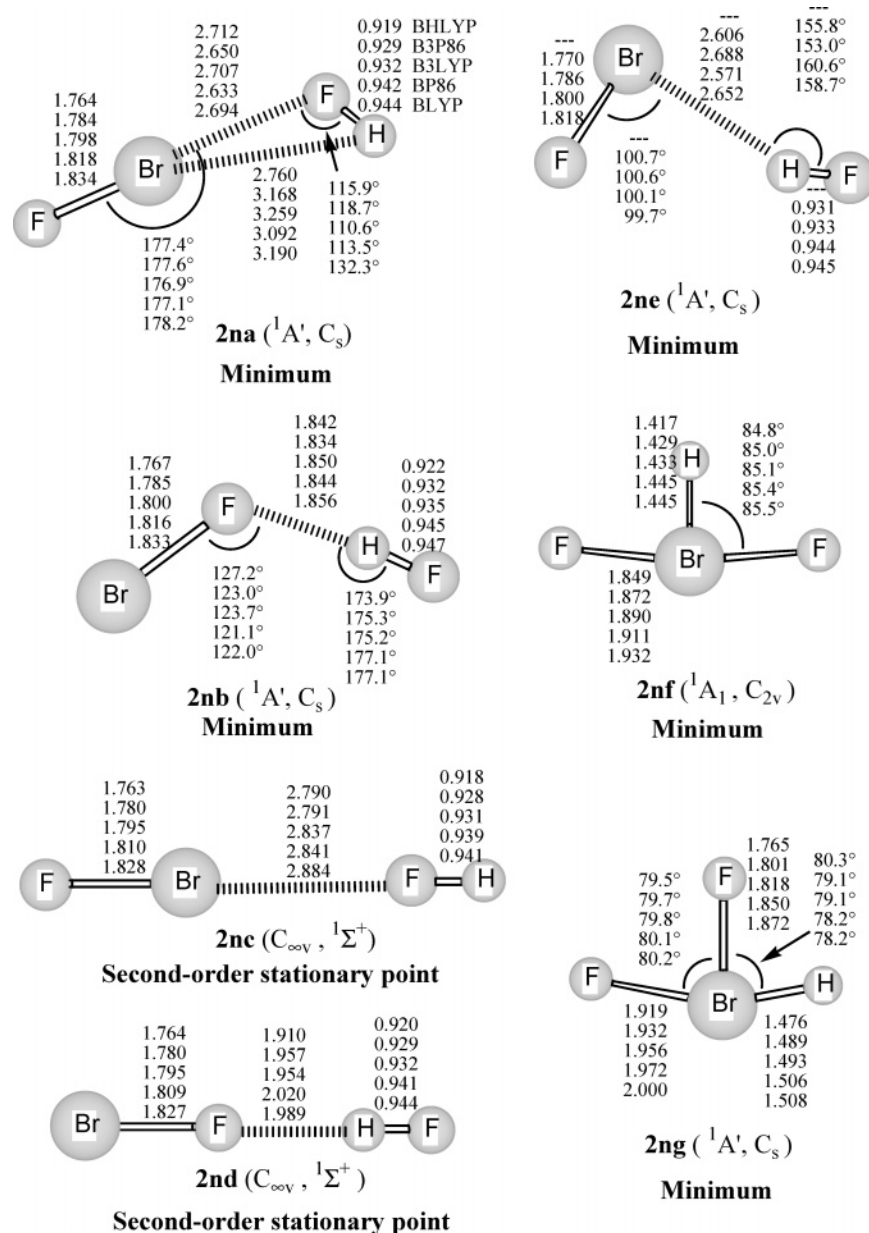
<sup>b</sup> Structure **4ac** with the BHLYP method is identical to that of **4aa**.

<sup>c</sup> Structure **4af** with the BLYP method collapses to **4ae**.

are listed in Table 2. The global minimum structure of BrF<sub>3</sub> has long been known to be T-shaped.<sup>12</sup> The mono-hydrogen analogue has two possible forms: a C<sub>2v</sub> structure with the central fluorine atom replaced by a hydrogen atom and a C<sub>s</sub> structure with the terminal fluorine atom replaced. Indeed, we found two corresponding minima, **2nf** and **2ng** analogous to the hyper-valent BrF<sub>3</sub>. They have normal Br–H and Br–F bond distances. The five methods predict the C<sub>2v</sub> structure (**2nf**) in its <sup>1</sup>A<sub>1</sub> electronic state to be similar to that for BrF<sub>3</sub>.<sup>9</sup> The Br–F bond distances in **2nf** are slightly (by about 0.05 Å) longer than those of BrF<sub>3</sub>, while the ∠HBrF bond angles are smaller than the corresponding ∠FBrF bond angle by 0.9–2.8°. Compared with the related C<sub>2v</sub> BrClF<sub>2</sub> structure, the Br–F bond distances of HBrF<sub>2</sub> are slightly longer than those in BrClF<sub>2</sub> (by about 0.02 Å), while the ∠HBrF bond angle is smaller than ∠ClBrF by 3.3–7.7°. The planar asymmetrical C<sub>s</sub> structure (**2ng**) with the <sup>1</sup>A' electronic state is also predicted to be a minimum. It lies energetically higher than that of **2nf** by 35 kcal/mol. The H–Br bond is ~0.05 Å longer than that in **2nf**. The F–Br bond lengths are also longer than the corresponding distances in BrF<sub>2</sub>.<sup>9</sup> However, neither of these two structures with normal Br–F and Br–H bonds is the global minimum, and there are several less conventional complexes that lie much lower in energy.

We have investigated two linear complexes, the stationary points FBr••FH (<sup>1</sup>Σ<sup>+</sup>, **2nc**) and BrF••HF (<sup>1</sup>Σ<sup>+</sup>, **2nd**). They have much lower energies than the BrF<sub>3</sub>-like structures but are predicted to be second-order stationary points, that is, points on the potential energy surface at which there are two imaginary harmonic vibrational frequencies. The doubly degenerate π imaginary vibrational modes lead to bent structures. Structure **2nc** collapses to **2na** (FBr••FH), which is the global minimum, lying energetically below the corresponding linear **2nc** structure by only 0.8 kcal/mol (B3LYP). Zero-point vibrational energies

- (14) The BHandLYP method implemented in the Gaussian programs has the formula, 0.5\*Ex(LSDA) + 0.5\*Ex(HF) + 0.5\*Delta-Ex(B88) + Ec(LYP), which is *not* precisely the formulation proposed by A. D. Becke in his paper, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
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**Figure 1.** Optimized structures for the neutral  $\text{HBrF}_2$  systems. Bond distances are in angstroms.

**Table 2.** Relative Energies in eV (or in kcal/mol in parentheses) for the Neutral  $\text{HBrF}_2$  System<sup>a</sup>

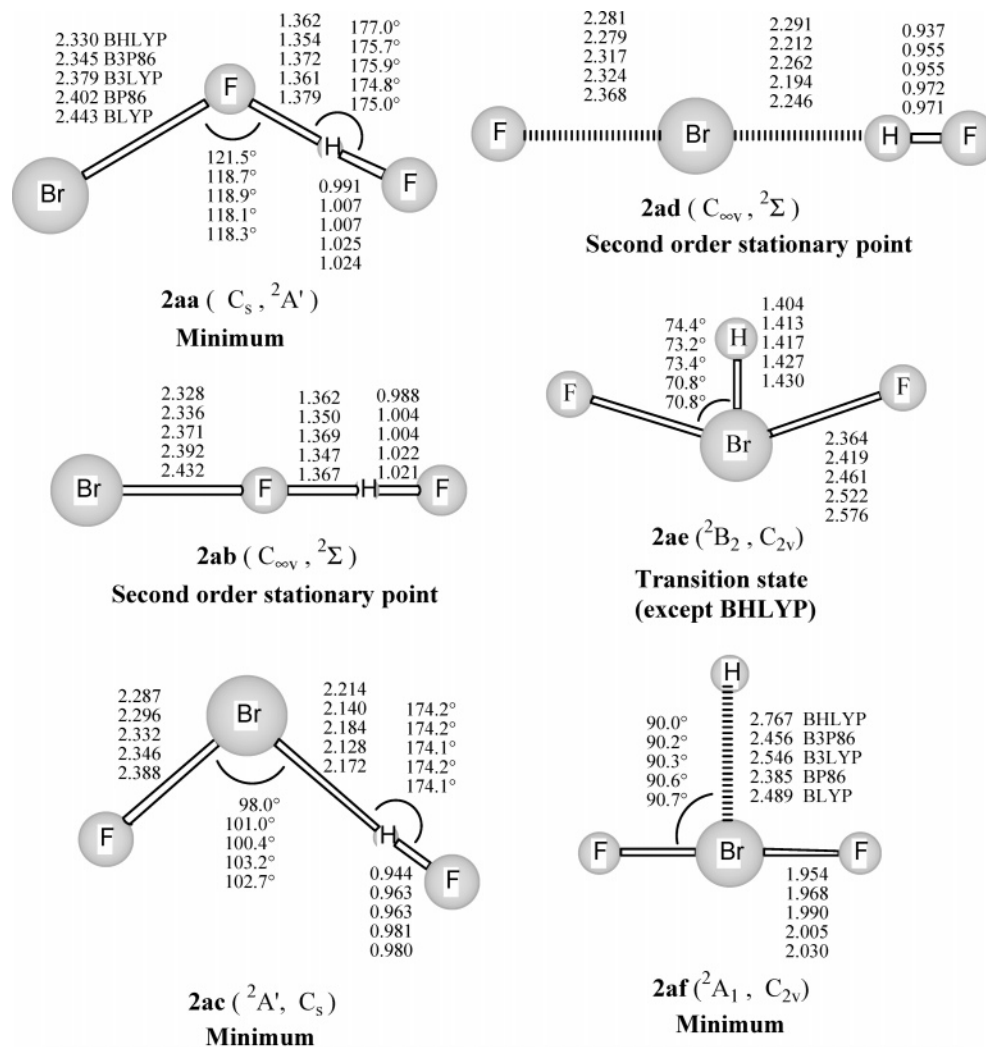
	BHLYP	B3P86	B3LYP	BP86	BLYP
H + BrF <sub>2</sub>	5.16 (119.0)	4.79 (110.5)	4.71 (108.6)	4.33 (99.8)	4.22 (97.4)
F + BrHF ( $^2\Sigma^+$ )	2.00 (46.2)	2.72 (62.8)	2.59 (59.8)	3.03 (69.8)	2.94 (67.7)
BrF + HF	0.16 (3.7)	0.15 (3.4)	0.15 (3.3)	0.11 (2.5)	0.14 (3.2)
<b>2na</b>	0.00	0.00	0.00	0.00	0.00
<b>2nb</b>	0.00 (0.0)	0.02 (0.5)	0.00 (0.1)	0.04 (0.9)	0.01 (0.2)
<b>2nc</b>	0.02 (0.6)	0.05 (1.1)	0.04 (0.8)	0.07 (1.5)	0.05 (1.2)
<b>2nd</b>	0.02 (0.5)	0.06 (1.4)	0.04 (0.9)	0.08 (1.9)	0.05 (1.2)
<b>2ne</b>	<i>b</i>	0.11 (2.5)	0.10 (2.4)	0.11 (2.5)	0.10 (2.3)
<b>2nf</b>	1.87 (43.1)	1.46 (33.7)	1.54 (35.5)	1.22 (28.2)	1.29 (29.7)
<b>2ng</b>	3.50 (80.7)	2.98 (68.7)	3.04 (70.2)	2.63 (60.7)	2.68 (61.9)

<sup>a</sup> Not corrected with ZPVE. <sup>b</sup> Structure **2ne** is not a stationary point with the BHLYP method.

do not reverse this qualitative prediction. Structure **2na** lies below **2nf** and **2ng** by 35 and 70 kcal/mol (B3LYP), respectively. It seems that complex **2na** is favored by the attraction of the negatively charged (in a simple picture) F atom (in H–F) and the positively charged Br atom (in Br–F). This phenomenon is analogous to that found for the neutral  $\text{Br}_2\text{F}_2$  molecule.<sup>24</sup> The

predicted dissociation energy of **2na** to HF + BrF is 3.3 kcal/mol (Table 2). Another bent structure **2nb** (BrF⋯HF), derived from **2nd**, lies slightly higher than that of **2na**. The nearly linear nonsymmetrical FH⋯F shape with a  $\sim 1.85$  Å H⋯F distance

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**Figure 2.** Optimized structures for the anionic  $\text{HBrF}_2^-$  systems. Bond distances are in angstroms.

**Table 3.** Relative Energies (in eV or in kcal/mol in parentheses) for the Anionic  $\text{HBrF}_2^-$  System<sup>a</sup>

	BHLYP	B3P86	B3LYP	BP86	BLYP
$\text{H}^- + \text{BrF}_2$	8.22 (189.7)	9.01 (207.8)	7.72 (178.0)	7.23 (166.8)	7.22 (166.5)
$\text{HF}^- + \text{BrF}$	4.87 (112.4)	4.84 (111.5)	4.82 (111.2)	4.72 (108.7)	4.76 (109.8)
$\text{H} + \text{BrF}_2^-$	4.06 (93.7)	3.89 (89.7)	3.84 (88.6)	3.68 (84.9)	3.61 (83.3)
$\text{F} + \text{BrHF}^-$	1.49 (34.4)	2.02 (46.7)	2.03 (46.8)	2.32 (53.6)	2.37 (54.7)
$\text{HF} + \text{BrF}^-$	1.20 (27.7)	1.20 (27.7)	1.18 (27.2)	1.17 (27.0)	1.16 (26.7)
$\text{Br} + \text{FHF}^-$	0.79 (18.3)	1.01 (23.4)	0.96 (22.2)	1.14 (26.3)	1.08 (24.9)
<b>2aa</b>	0.00	0.00	0.00	0.00	0.00
<b>2ab</b>	0.05 (1.1)	0.08 (1.7)	0.07 (1.6)	0.09 (2.0)	0.09 (1.9)
<b>2ac</b>	0.52 (12.1)	0.49 (11.3)	0.49 (11.4)	0.46 (10.7)	0.47 (10.9)
<b>2ad</b>	0.66 (15.3)	0.63 (14.6)	0.64 (14.7)	0.61 (14.0)	0.62 (14.2)
<b>2ae</b>	3.34 (77.0)	2.97 (68.6)	2.92 (67.4)	2.65 (61.0)	2.58 (59.5)
<b>2af</b>	4.03 (92.9)	3.80 (87.6)	3.77 (87.0)	3.55 (81.8)	3.51 (81.0)

<sup>a</sup> Not corrected with ZPVE.

suggests a weak but conventional hydrogen bond between the two fragments in **2nb**. Accordingly, the dissociation energy (to  $\text{HF} + \text{BrF}$ ) for **2nb** is 3.2 kcal/mol (Table 2).

The other planar  $C_s$  structure  $\text{FBr}\cdots\text{HF}$  (**2ne**) is predicted to be a local minimum at four DFT levels (except for BHLYP, which predicts dissociation to  $\text{HF} + \text{BrF}$ ). Structure **2ne** lies energetically above the global minimum by  $\sim 2.4$  kcal/mol (Table 2). The interaction between the  $\text{FBr}$  and  $\text{HF}$  fragments in **2ne** is weak, with the dissociation energy (to  $\text{FBr} + \text{HF}$ ) being 0.9 kcal/mol (Table 2).

In summary, three complexes (**2na**, **2nb**, and **2ne**) have energies within 3 kcal/mol, while structures **2nf** and **2ng** with normal  $\text{Br}-\text{H}$  and  $\text{Br}-\text{F}$  bonds have significantly higher energies than the global minimum, by 35 kcal/mol for **2nf** and 70 kcal/mol for **2ng** (Table 2).

The optimized equilibrium geometries for anionic  $\text{HBrF}_2^-$  are shown in Figure 2 (**2aa**–**2af**), and their relative energies are listed in Table 3. The linear structure with strong hydrogen bonding  $[\text{Br}\cdots\text{FHF}]^-$  (**2ab**) is predicted to be a second-order stationary point, the doubly degenerate imaginary vibrational



modes leading to the planar  $C_s$  structure  $[\text{Br}\cdots\text{FHF}]^-$  (**2aa**) in its  ${}^2A'$  state with a hydrogen bond. The isolated  $\text{FHF}^-$  anion is known to be relatively stable. Structure **2aa** is the global minimum, but it lies only 1.6 kcal/mol below **2ab** (B3LYP, Table 3). Compared with the analogous neutral structure **2nb**, structure **2aa** has a much shorter  $\text{F}\cdots\text{H}$  distance than that in **2nb** (by  $\sim 0.5$  Å), and the  $\text{Br}-\text{F}$  distance of **2aa** is much longer than that of **2nb** (by 0.6 Å), indicating a stronger hydrogen bond. Accordingly, the dissociation energy to  $\text{HF} + \text{BrF}^-$  is  $\sim 27$  kcal/mol, which is almost eight times that for the analogous neutral **2nb**. Another linear structure  $[\text{F}\cdots\text{Br}\cdots\text{HF}]^-$  (**2ad**) is also a second-order stationary point, lying 15 kcal/mol above **2aa**. The modes of the imaginary vibrational frequencies lead to another planar  $C_s$  structure (**2ac**), which is a local minimum lying 11 kcal/mol higher than the global minimum. The linear  $\text{Br}\cdots\text{HF}$  structure **2ac** could be thought of as a weak hydrogen bonding situation with the  $\text{Br}\cdots\text{H}$  distance  $\sim 2.2$  Å. Compared with this, the corresponding neutral structure **2ne** has even weaker interaction between the fragments  $\text{FBr}$  and  $\text{HF}$ , with the  $\text{Br}\cdots\text{H}$  distance as long as  $\sim 2.6$  Å.

Like the neutrals, the Br-centered structures have higher energies. The  $C_{2v}$  structure **2ae** is a transition state (except with BHLYP, which predicts a minimum). Compared to its neutral analogue **2nf**, the  $\text{Br}-\text{H}$  bond distance is similar, but its  $\text{Br}-\text{F}$  bonds ( $\sim 2.36$  Å, BHLYP) are much longer (by  $\sim 0.5$  Å). Following the imaginary frequency mode ( $b_2$ ) leads to structure **2ac**. Another  $C_{2v}$  structure ( ${}^2A_1$ , **2af**), although with higher energy, is predicted to be a minimum with two normal  $\text{Br}-\text{F}$  bonds (1.95 Å) and a very long  $\text{H}-\text{Br}$  distance (2.77 Å). When adding one electron to the neutral **2nf** ( $C_{2v}$ ,  ${}^1A_1$ ), there are two related anionic structures **2ae** ( $C_{2v}$ ,  ${}^2B_2$ ) and **2af** ( $C_{2v}$ ,  ${}^2A_1$ ). The former has long  $\text{Br}-\text{F}$  bonds, and the latter has a very long  $\text{Br}-\text{H}$  bond, indicating that the singly-occupied molecular orbitals are antibonding orbitals either for the  $\text{Br}-\text{F}$  bonds ( $b_2$ ) or for the  $\text{Br}-\text{H}$  bond ( $a_1$ ). The energy of **2ae** is higher than that of **2aa** by 67 kcal/mol, while the energy of **2af** is higher by 87 kcal/mol. Compared with the energy of the dissociation limit  $\text{BrF}_2^- + \text{H}$  (89 kcal/mol, in Table 3, B3LYP), the energy of complex **2af** is only 2 kcal/mol lower (Table 3), and it may dissociate easily. Because the  $\text{F}-\text{H}\cdots\text{F}$  bonds are stronger than the  $\text{H}\cdots\text{Br}$  and  $\text{F}\cdots\text{Br}$  interactions, the Br-centered geometry should have the higher energy.

Generally, the theoretical bond lengths falls in the order of  $\text{BHLYP} < \text{B3P86} < \text{B3LYP} < \text{BP86} < \text{BLYP}$ , like those for the isolated  $\text{BrF}$ ,  $\text{HF}$ , and  $\text{HBr}$  molecules. Experience suggests that the BHLYP structures are the most reliable for these interhalogen compounds.<sup>9</sup>

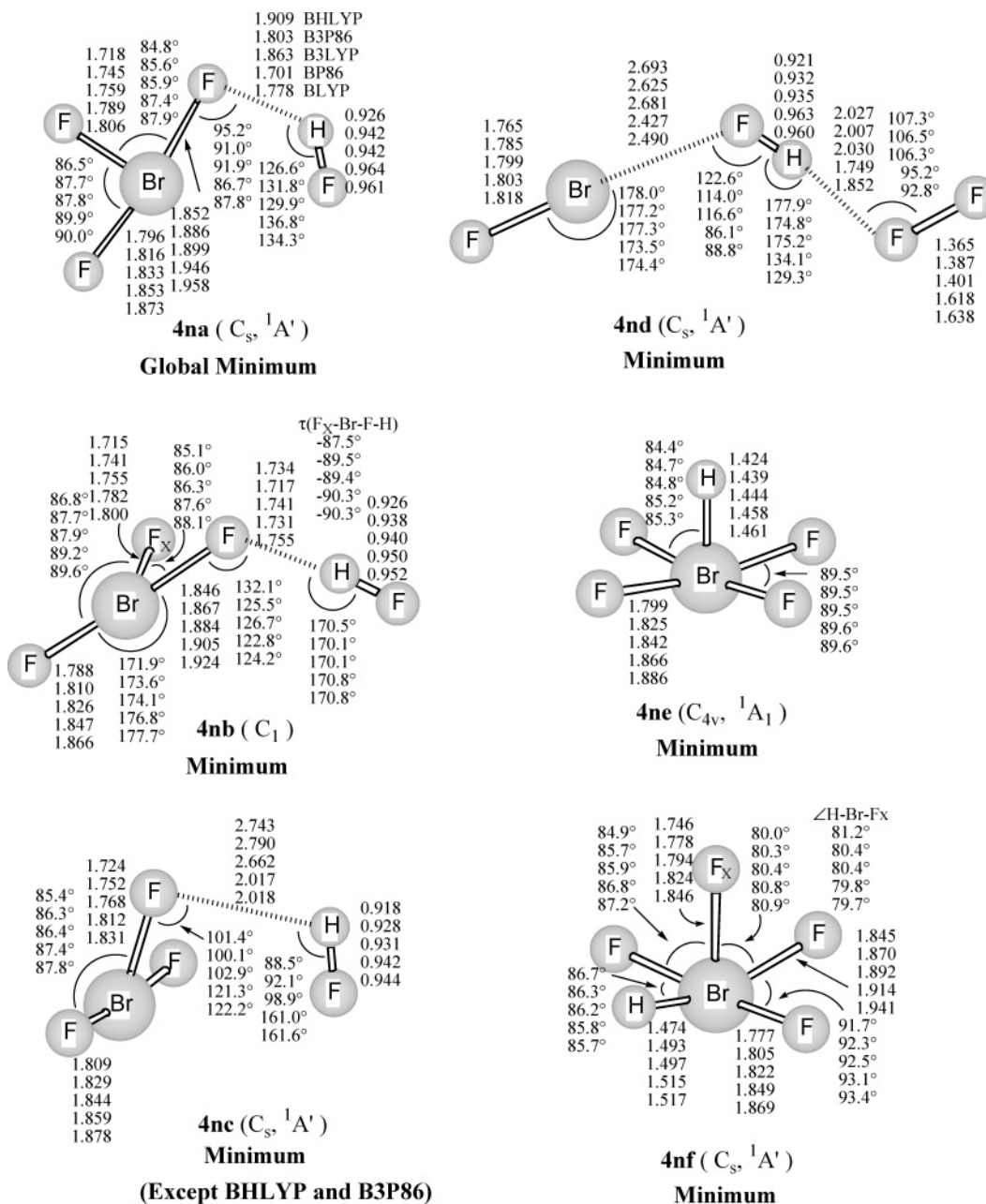
**2.  $\text{HBrF}_4/\text{HBrF}_4^-$ .** The global minimum of  $\text{BrF}_5$  has  $C_{4v}$  symmetry,<sup>13</sup> with two distinguishable kinds of fluorine atoms (axial and equatorial), either of which might be substituted by a hydrogen atom. These two  $\text{HBrF}_4$  isomers (**4ne** and **4nf**) were found, possessing normal  $\text{Br}-\text{F}$  and  $\text{Br}-\text{H}$  bonds. Structure **4ne**  $\text{HBrF}_4$  has  $C_{4v}$  symmetry ( ${}^1A_1$  state, Figure 3). The  $\text{Br}-\text{H}$  distances are 1.42 Å (axial) and 1.47 Å (equatorial), and the  $\text{Br}-\text{F}$  bonds range from 1.75 Å (axial) and 1.80 Å (equatorial, **4ne**) to 1.78 (axial) and 1.85 Å (equatorial, **4nf**). The DFT  $\text{Br}-\text{F}$  bonds in **4ne** are slightly longer than those in  $\text{BrF}_5$ , by 0.03 Å.<sup>9</sup> Similarly, the  $\text{Br}-\text{F}$  distances in the corresponding  $\text{ClBrF}_4$  structure<sup>8</sup> are longer than those in  $\text{BrF}_5$  by 0.02 Å. This is understandable because for  $\text{HBrF}_4$  and  $\text{ClBrF}_4$  more electron

density is located in the  $\text{FBrF}$  vicinity (F is more electronegative than H and Cl), and the highest occupied molecular orbital is an antibonding orbital. The other  $\text{HBrF}_4$  isomer with normal  $\text{Br}-\text{H}$  and  $\text{Br}-\text{F}$  bonds is **4nf** (Figure 3). Because an equatorial F atom was replaced by an H atom, **4nf** has  $C_s$  symmetry in its  ${}^1A'$  electronic ground state. Compared with the  $C_{4v}$  structure **4ne**, the  $\text{Br}-\text{H}$  bond length of **4nf** is longer by  $\sim 0.05$  Å, the  $\text{Br}-\text{F}$  bond opposite to  $\text{Br}-\text{H}$  is longer, and the other three  $\text{Br}-\text{F}$  bonds are shorter. The energy of **4nf** is higher than **4ne** by 26 kcal/mol (Table 3). Similar to  $\text{HBrF}_2$ , structures **4ne** and **4nf** are not global minima, and the more stable species are the  $\text{HBrF}_4$  complexes (**4na**–**4nd**).

The global minimum for  $\text{HBrF}_4$  is a planar  $\text{F}_2\text{BrF}\cdots\text{HF}$  structure (**4na**) with  $C_s$  symmetry. **4na** is a complex of  $\text{BrF}_3$  and  $\text{HF}$ , connected by an  $\text{F}\cdots\text{HF}$  hydrogen bond. The energy of **4na** is lower than that of **4ne** by 54 kcal/mol. The  $\text{F}\cdots\text{HF}$  hydrogen bond distance (1.91 Å) is slightly longer than that for **2nb** (1.84 Å). The  $\angle\text{F}\cdots\text{HF}$  angle for **4na** is  $127^\circ$ , much smaller than the analogous angle in **2nb**, which is nearly linear. The dissociation energy of the complex **4na** to  $\text{BrF}_3 + \text{HF}$  is about 5.6 kcal/mol (Table 3), which is larger than that for **2nb**. When the  $\text{BrF}_3$  fragment rotates by  $\sim 90^\circ$ , a  $C_1$  minimum (**4nb**) is obtained. With a few exceptions, all the internuclear distances (including the  $\text{F}\cdots\text{H}$  distance) in **4nb** are slightly shorter than those in **4na**. The  $\angle\text{F}-\text{H}\cdots\text{F}$  angle is  $\sim 170^\circ$ . The energy of **4nb** is close to that of the global minimum **4na** (within 0.5 kcal/mol, B3LYP). The dissociation energy of **4nb** to  $\text{BrF}_3 + \text{HF}$  is predicted to be 5.1 kcal/mol.

The nonplanar  $\text{F}_2\text{BrF}\cdots\text{FH}$  structure **4nc** is predicted to be a minimum (except with the BHLYP and B3P86 methods, which predict a transition state that eventually collapses to **4nb**). The  $\text{F}\cdots\text{H}$  distance in **4nc** is quite long ( $\sim 2.0$  Å from the pure DFT methods;  $\sim 2.7$  Å from the hybrid methods), and the  $\angle\text{F}\cdots\text{HF}$  angle is quite small ( $\sim 161^\circ$  from the pure DFT methods;  $\sim 90^\circ$  from the hybrid methods, Figure 3). Structure **4nc** lies above the global minimum **4na** by 4 kcal/mol. **4nc** is predicted to lie below  $\text{HF} + \text{BrF}_3$  by only 1.4 kcal/mol (Table 4). Structure **4nd** is an unusual complex of the form  $\text{FBr}\cdots\text{FH}\cdots\text{F}_2$ . There appears a weak hydrogen bond between  $\text{F}-\text{H}$  and  $\text{F}_2$  and a dipole-induced interaction between  $\text{FBr}$  and  $\text{FH}$ . **4nd** could also be considered as a complex of **2na** with  $\text{F}_2$ , but with a slightly longer  $\text{F}-\text{H}$  distance and a shorter  $\text{Br}\cdots\text{F}$  distance. The geometry differences are dependent on the methods, hybrid or pure DFT. The energy of **4nd** is higher than that of **4na** by 46 kcal/mol, and this energy is only 4 kcal/mol (hybrid methods) lower than the dissociation limit  $\text{FBr} + \text{FH} + \text{F}_2$  (Table 4).

The predicted anionic  $\text{HBrF}_4^-$  structures are shown in Figure 4, and the relative energies are reported in Table 5. The global minimum for anionic  $\text{HBrF}_4^-$  has a nonplanar  $C_s$  structure (**4aa**). It may be regarded as a complex of  $[\text{F}_2\text{Br}\cdots\text{F}]^- \cdots \text{HF}$  with a strong  $\text{F}\cdots\text{HF}$  hydrogen bond. Compared with the corresponding neutral structure **4nc**, the anion has the stronger hydrogen bond, because of the shorter  $\text{F}\cdots\text{H}$  distance (1.47 Å), slightly longer  $\text{H}-\text{F}$  distance (0.96 Å), and nearly linear  $\text{F}\cdots\text{HF}$  linkage. The dissociation energy to  $\text{BrF}_3^- + \text{HF}$  is more than 20 kcal/mol (Table 5). This large dissociation energy is consistent with its stability as a global minimum. Structure **4ab** has a similar geometry to **4aa**, with a slightly longer  $\text{H}\cdots\text{F}$  distance and accordingly a slightly higher ( $< 4.0$  kcal/mol) energy (except BHLYP, which predicts a shorter  $\text{H}\cdots\text{F}$  distance



**Figure 3.** Optimized structures for the neutral HBrF<sub>4</sub> systems. Bond distances are in angstroms.

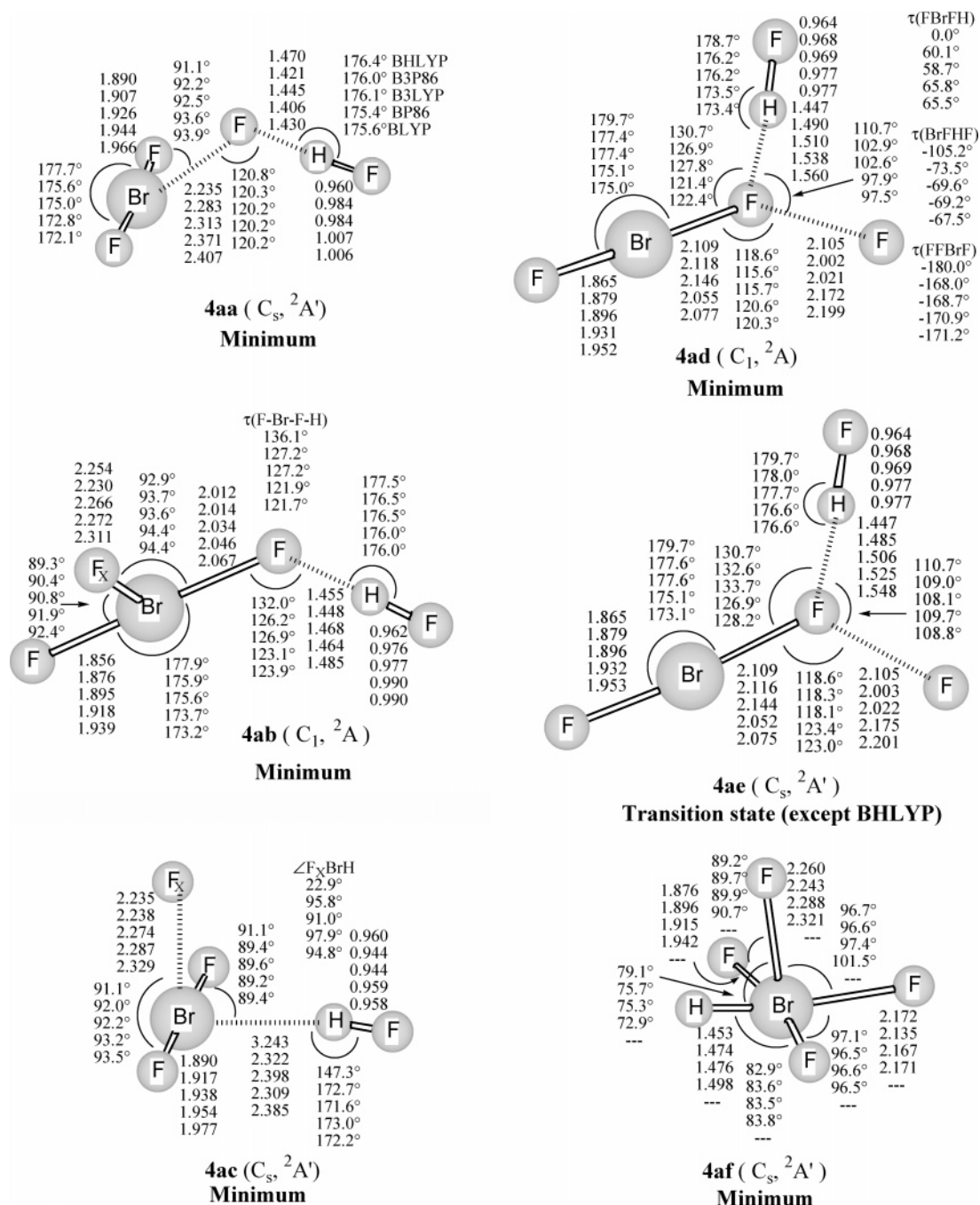
**Table 4.** Relative Energies in EV (or in kcal/mol in parentheses) for the Neutral HBrF<sub>4</sub> System<sup>a</sup>

	BHLYP	B3P86	B3LYP	BP86	BLYP
H + BrF <sub>4</sub>	5.50 (126.8)	5.08 (117.1)	5.02 (115.8)	4.59 (105.8)	4.51 (103.9)
HBrF + F <sub>3</sub>	3.79 (87.5)	4.89 (112.7)	4.64 (107.0)	5.36 (123.7)	5.17 (119.1)
BrF + HF + F <sub>2</sub>	1.94 (44.7)	2.29 (52.8)	2.17 (49.9)	2.47 (56.9)	2.37 (54.6)
F + BrHF <sub>3</sub>	1.71 (39.4)	2.33 (53.7)	2.14 (49.3)	2.52 (58.1)	2.35 (54.2)
F <sub>2</sub> + HBrF <sub>2</sub>	1.78 (41.0)	2.14 (49.3)	2.02 (46.6)	2.32 (53.6)	2.23 (51.4)
HF + BrF <sub>3</sub>	0.27 (6.1)	0.24 (5.6)	0.24 (5.6)	0.24 (5.6)	0.24 (5.4)
<b>4na</b>	0.0	0.0	0.0	0.0	0.0
<b>4nb</b>	0.02 (0.4)	0.03 (0.8)	0.02 (0.5)	0.06 (1.4)	0.04 (0.9)
<b>4nc</b>	0.18 (4.1)	0.19 (4.4)	0.18 (4.2)	0.20 (4.7)	0.18 (4.1)
<b>4nd</b>	1.73 (39.9)	2.11 (48.6)	1.98 (45.6)	1.94 (44.7)	1.81 (41.7)
<b>4ne</b>	2.67 (61.7)	2.24 (51.7)	2.35 (54.2)	2.03 (46.8)	2.13 (49.2)
<b>4nf</b>	3.85 (88.7)	3.37 (77.6)	3.49 (80.4)	3.10 (71.5)	3.21 (74.0)

<sup>a</sup> Not corrected with ZPVE.

and a lower energy; see Table 5). The dissociation energy of anion **4ab** to BrF<sub>3</sub><sup>-</sup> + HF is about 19 kcal/mol, which is comparable with that for **2ac** dissociating to BrF<sup>-</sup> + HF (~17

kcal/mol, Table 3). A nonplanar C<sub>s</sub> structure F<sub>3</sub>Br...HF (**4ac**) with long Br...H distance is a minimum for all five DFT methods except BHLYP, with which structure **4ac** is not close



**Figure 4.** Optimized structures for the anionic  $\text{HBrF}_4^-$  systems. Bond distances are in angstroms.

to the geometries predicted by other methods, but collapses to **4aa**. The energy of **4ac** is higher than that of **4aa** by 12–13 kcal/mol.

The planar  $C_s$  stationary **4ae** is composed of  $\text{FBrF}^-(\cdots\text{F})\cdots\text{HF}$  (Figure 4). The  $\text{F}\cdots\text{HF}$  arrangement in **4ae** suggests a strong hydrogen bond. The energy of **4ae** is higher than that of **4aa** by 15 kcal/mol (Table 5). Structure **4ae** is predicted to be a transition state. The mode of the imaginary frequency leads to a minimum with  $C_1$  structure (**4ad**), which is only slightly distorted from **4ae** and lies slightly lower in energy than **4ae** (Table 5).

There is no low-lying structure of  $\text{HBrF}_4^-$  analogous to neutral  $\text{BrF}_5$  or the  $\text{BrF}_5^-$  anion. The  $C_s$  structure **4af** has geometry similar to that of the neutral **4nf** but with the all  $\text{Br}-\text{F}$  bond distances longer. Structure **4af** lies above **4aa** by 87 kcal/mol.

Structure **4af** predicted by the BLYP method is not a stationary point and collapses to **4ac**. The anionic  $\text{HBrF}_4^-$  structure with  $C_{4v}$  symmetry (not shown in Figure 4) has a very long  $\text{H}\cdots\text{Br}$  distance (3.3 Å, BHLYP) and a very high energy ( $\sim 90$  kcal/mol above **4aa**), so it will not be discussed further.

**3. Electron Affinities.** The DFT predicted neutral–anion energy separations for  $\text{HBrF}_2/\text{HBrF}_2^-$  and  $\text{HBrF}_4/\text{HBrF}_4^-$  are listed in Table 6. The adiabatic electron affinity  $\text{EA}_{\text{ad}}$  is the energy difference between the *global minima*, that is,  $2\text{na} \leftarrow 2\text{aa}$  for  $\text{HBrF}_2$  and  $4\text{na} \leftarrow 4\text{aa}$  for  $\text{HBrF}_4$ . But we also list in Table 6 the energy differences between some *local minima* (neutral and anion). Because of their geometrical similarity, such as  $2\text{nf} \leftarrow 2\text{ae}$  or  $4\text{nf} \leftarrow 4\text{af}$ , these local electron affinities are more likely to be observable experimentally.

**Table 5.** Relative Energies in eV (or in kcal/mol in parentheses) for the Anionic HBrF<sub>4</sub><sup>-</sup> System<sup>a</sup>

	BHLYP	B3P86	B3LYP	BP86	BLYP
H <sup>-</sup> + BrF <sub>4</sub>	9.26 (213.5)	8.72 (201.0)	8.76 (202.0)	8.14 (187.8)	8.25 (190.2)
BrF + HF <sup>-</sup> + F <sub>2</sub>	7.35 (169.5)	7.63 (175.9)	7.58 (174.7)	7.69 (177.3)	7.74 (178.4)
HF <sup>-</sup> + BrF <sub>3</sub>	5.68 (130.9)	5.59 (128.8)	5.65 (130.3)	5.46 (126.1)	5.60 (129.2)
HBrF <sup>-</sup> + F <sub>3</sub>	3.95 (91.1)	4.81 (111.0)	4.78 (110.1)	5.30 (122.2)	5.34 (123.2)
H + BrF <sub>4</sub> <sup>-</sup>	4.30 (99.1)	4.03 (93.0)	4.02 (92.6)	3.81 (87.8)	3.78 (87.1)
BrF <sup>-</sup> + HF + F <sub>2</sub>	3.68 (84.8)	3.99 (92.0)	3.93 (90.6)	4.15 (95.6)	4.13 (95.3)
F <sup>-</sup> + BrHF <sub>3</sub>	3.15 (72.7)	3.27 (75.4)	3.18 (73.4)	3.24 (74.6)	3.17 (73.0)
BrF + HF + F <sub>2</sub> <sup>-</sup>	2.81 (64.8)	3.19 (73.5)	3.03 (69.8)	3.32 (76.6)	3.18 (73.3)
F <sub>2</sub> <sup>-</sup> + HBrF <sub>2</sub>	2.65 (61.1)	3.04 (70.1)	2.88 (66.5)	3.18 (73.3)	3.04 (70.1)
F <sub>2</sub> + HBrF <sub>2</sub> <sup>-</sup>	2.47 (57.0)	2.79 (64.4)	2.75 (63.4)	2.97 (68.6)	2.97 (68.6)
FHF <sup>-</sup> + BrF <sub>2</sub>	1.34 (30.8)	1.58 (31.7)	1.36 (31.3)	1.36 (31.5)	1.35 (31.1)
F + BrHF <sub>3</sub> <sup>-</sup>	0.48 (11.1)	1.24 (28.7)	1.19 (27.5)	1.70 (39.3)	1.68 (38.8)
HF + BrF <sub>3</sub> <sup>-</sup>	0.87 (20.0)	0.95 (21.9)	0.93 (21.3)	0.97 (22.5)	0.96 (22.0)
<b>4aa</b>	0.0	0.0	0.0	0.0	0.0
<b>4ab</b>	-0.04 (-0.9)	0.10 (2.2)	0.08 (1.8)	0.17 (4.0)	0.16 (3.6)
<b>4ac</b>	0.00	0.54 (12.4)	0.53 (12.2)	0.57 (13.2)	0.57 (13.1)
<b>4ad</b>	0.31 (6.3)	0.75 (17.1)	0.66 (15.2)	0.83 (19.3)	0.77 (17.6)
<b>4ae</b>	0.31 (6.3)	0.75 (17.2)	0.66 (15.3)	0.84 (19.5)	0.78 (17.8)
<b>4af</b>	4.11 (94.7)	3.77 (86.9)	3.77 (86.9)	3.44 (79.5)	<i>b</i>

<sup>a</sup> Not corrected with ZPVE. <sup>b</sup> Collapsed to **4ac** at BLYP.

**Table 6.** Adiabatic Electron Affinities EA<sub>ad</sub> and EA<sub>ad(ZPVE)</sub> (with and without ZPVE corrections), Vertical Electron Affinities (EA<sub>vert</sub>) for the Neutral HBrF<sub>2</sub> and HBrF<sub>4</sub> Species, and VDEs for the Anionic HBrF<sub>2</sub><sup>-</sup> and HBrF<sub>4</sub><sup>-</sup> Species in eV (or in kcal/mol in parentheses) Predicted by Five DFT Methods with DZP++ Basis Sets

compound	method	EA <sub>ad</sub>	EA <sub>ad(ZPVE)</sub>	EA <sub>vert</sub>	VDE
<b>2na–2aa</b> ( <sup>1</sup> A'– <sup>2</sup> A')	BHLYP	3.69 (85.0)	3.67 (84.7)	0.51 (11.7)	5.72 (132.0)
	B3P86	4.34 (102.2)	4.42 (102.0)	1.34 (30.9)	6.11 (141.0)
	B3LYP	3.86 (89.0)	3.85 (88.8)	0.97 (22.3)	5.62 (129.6)
	BP86	3.91 (90.2)	3.91 (90.1)	1.13 (26.1)	5.38 (124.0)
	BLYP	3.77 (86.8)	3.76 (86.7)	1.10 (25.3)	5.24 (120.9)
<b>4na–4aa</b> ( <sup>1</sup> A'– <sup>2</sup> A')	BHLYP	4.38 (101.8)	4.45 (102.7)	1.79 (41.3)	6.62 (152.7)
	B3P86	4.96 (114.2)	5.00 (115.2)	2.56 (59.0)	6.80 (156.7)
	B3LYP	4.49 (105.7)	4.62 (106.6)	2.20 (50.8)	6.37 (146.8)
	BP86	4.48 (103.5)	4.54 (104.6)	2.28 (52.6)	5.89 (135.8)
	BLYP	4.49 (103.5)	4.53 (104.5)	2.30 (53.1)	5.81 (134.0)
compound	method	local EA	local EA <sub>(ZPVE)</sub>	EA <sub>vert</sub>	VDE
<b>2nb–2aa</b> ( <sup>1</sup> A'– <sup>2</sup> A')	BHLYP	3.69 (85.0)	3.70 (85.2)	1.83 (42.2)	5.72 (132.0)
	B3P86	4.32 (99.7)	4.33 (99.9)	2.60 (59.9)	6.11 (141.0)
	B3LYP	3.86 (89.0)	3.87 (89.2)	2.15 (49.5)	5.62 (129.6)
	BP86	3.87 (89.3)	3.88 (89.6)	2.26 (52.2)	5.38 (124.0)
	BLYP	3.76 (86.6)	3.77 (86.9)	2.16 (49.9)	5.24 (120.9)
<b>2nf–2ae</b> ( <sup>1</sup> A <sub>1</sub> – <sup>2</sup> B <sub>2</sub> )	BHLYP	2.22 (51.2)	2.30 (53.1)	-0.52 (-12.1)	4.92 (113.4)
	B3P86	2.79 (64.3)	2.89 (66.7)	0.31 (7.1)	5.26 (121.5)
	B3LYP	2.47 (57.0)	2.58 (59.4)	0.02 (0.4)	4.91 (113.2)
	BP86	2.41 (55.6)	2.51 (57.9)	-0.34 (-7.8)	4.72 (108.8)
	BLYP	2.45 (56.7)	2.55 (59.0)	-0.01 (-0.3)	4.72 (108.8)
<b>4na–4ab</b> ( <sup>1</sup> A'– <sup>2</sup> A)	BHLYP	4.42 (102.0)	4.47 (103.1)	1.79 (41.3)	6.83 (157.6)
	B3P86	4.86 (112.0)	4.90 (113.0)	2.56 (59.0)	6.67 (153.8)
	B3LYP	4.51 (103.9)	4.55 (104.8)	2.20 (50.8)	6.28 (144.9)
	BP86	4.32 (99.5)	4.36 (100.5)	2.28 (52.6)	6.08 (140.1)
	BLYP	4.33 (99.9)	4.37 (100.8)	2.30 (53.1)	5.70 (131.3)
<b>4nf–4af</b> ( <sup>1</sup> A'– <sup>2</sup> A')	BHLYP	4.13 (95.1)	4.25 (98.0)	1.73 (39.8)	6.88 (158.6)
	B3P86	4.55 (105.0)	4.66 (107.4)	2.64 (60.8)	6.46 (149.1)
	B3LYP	4.30 (99.2)	4.41 (101.6)	2.40 (55.4)	6.16 (142.2)
	BP86	4.14 (95.5)	4.24 (97.9)	2.55 (58.8)	5.65 (130.4)
	BLYP <sup>a</sup>				

<sup>a</sup> At the BLYP level, structure **4af** collapses to **4ac**.

Among the five DFT methods, B3P86 spuriously predicts EA<sub>ad</sub> values significantly higher, while the other four methods predict electron affinities in reasonable agreement with each other. Previous studies<sup>8,9,19</sup> have shown that the BHLYP method appears to be the best in the predictions of the electron affinities of the interhalogens. With the BHLYP method, the EA<sub>ad</sub> for HBrF<sub>2</sub> is 3.69 eV and that for HBrF<sub>4</sub> is 4.38 eV (Table 6). After ZPVE correction, the EA<sub>ad(ZPVE)</sub> values are 3.67 and 4.45 eV, respectively. There are no experimental or previous theoretical

studies, but we can compare the present results with the related molecules ClBrF<sub>n</sub>, Br<sub>2</sub>F<sub>n</sub>, and BrF<sub>n+1</sub>. From Table 7, we can see that the electron affinities of these related molecules are comparable, with the trend EA<sub>ad</sub>(HBrF<sub>2</sub>) < EA<sub>ad</sub>(BrF<sub>3</sub>) < EA<sub>ad</sub>(Br<sub>2</sub>F<sub>2</sub>) ~ EA<sub>ad</sub>(ClBrF<sub>2</sub>) and EA<sub>ad</sub>(BrF<sub>5</sub>) < EA<sub>ad</sub>(HBrF<sub>4</sub>) < EA<sub>ad</sub>(Br<sub>2</sub>F<sub>4</sub>) < EA<sub>ad</sub>(ClBrF<sub>4</sub>). This is quite understandable because the electron affinities of these elements fall in the order H ≪ F ~ Br < Cl,<sup>25</sup> with the latter three halogens having rather similar electron affinities. All the predicted electron affinities



**Table 7.** Comparison of the Adiabatic Electron Affinities  $EA_{ad}$  (without ZPVE Correction, in eV) of  $HBrF_n$  ( $n = 2, 4$ ) with  $Br_2F_n$ ,  $BrClF_n$ , and  $BrF_n$  with the DZP++ BHLYP Method<sup>a</sup>

$n$	$HBrF_n$	$Br_2F_n^a$	$BrClF_n^b$	$BrF_{n+1}^c$
2	3.69	4.35	4.35	3.77
4	4.38	4.49	5.25	4.24

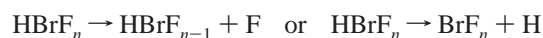
<sup>a</sup> Reference 24. <sup>b</sup> Reference 8. <sup>c</sup> Reference 9.

are substantial, suggesting that these anion complexes  $HBrF_2^-$  and  $HBrF_4^-$  may exist in the laboratory.

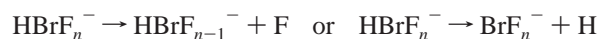
The local electron affinity value for  $2nb \leftarrow 2aa$  is almost the same as the global electron affinity, because the energy of  $2nb$  is close to that of  $2na$ . The local electron affinity for  $4na \leftarrow 4ab$  displays a similar situation. The local electron affinities for  $2nf \leftarrow 2ae$  and  $4nf \leftarrow 4af$  refer to the neutral and anionic structures with all normal Br–F and Br–H bonds, instead of the lower energy complexes. The local electron affinity for  $2nf \leftarrow 2ae$  (2.22 eV, BHLYP) is smaller than  $EA_{ad}(2na \leftarrow 2aa)$ , while the local electron affinity for  $4nf \leftarrow 4af$  (4.13 eV, BHLYP) is close to  $EA_{ad}(4na \leftarrow 4aa)$ .

The vertical electron affinities ( $EA_{vert}$ ) and VDE are also listed in Table 6. It is seen that the  $EA_{vert}$  and VDE values for  $HBrF_2$  and  $HBrF_4$  are quite different because of the significant differences between the neutral and anionic geometries.

**4. Dissociation Energies.** The dissociation energies for the  $HBrF_n/HBrF_n^-$  complexes to their fragments have already been discussed. In this section, we will pay attention to the first fluorine and first hydrogen dissociation energies. For the neutral species, the first dissociation energies refer to the reactions



For the anions, the first dissociation energies refer to two different reactions. One involves release of a neutral F or H atom:



The second dissociation process involves release a  $F^-$  or  $H^-$  anion:



The predicted dissociation energies are presented in Table 8. As pointed out in previous studies,<sup>8,9,19,24</sup> the BHLYP results are least reliable for dissociation energies and will not be discussed hereafter. The other DFT methods predict first

dissociation energies in reasonable agreement with each other, although the pure DFT methods (BP86 and BLYP) yield somewhat larger  $D_e$  values than the hybrid methods (B3P86 and B3LYP). There are no experimental results for comparison, but the B3LYP prediction may be considered the most dependable.<sup>6</sup> It is seen that the first dissociation energy for the neutral  $HBrF_2$  and  $HBrF_4$  species are significantly high, for example,  $D_e(BrHF-F) = 60$  kcal/mol and  $D_e(BrF_2-H) = 109$  kcal/mol (B3LYP) for **2na** and  $D_e(BrHF_3-F) = 49$  kcal/mol and  $D_e(BrF_4-H) = 116$  kcal/mol for **4na** (Table 8). These large values (especially for dissociation to a hydrogen atom) indicate that the  $HBrF_2$  and  $HBrF_4$  species are thermodynamically stable with respect to fluorine atom or hydrogen atom dissociation. For the anionic species, the dissociation energies are also significantly high. The pathways to  $HBrF_{n-1} + F^-$  have higher barriers than the routes to  $HBrF_{n-1}^- + F$ , while the differences between the pathways to  $BrF_n + H^-$  and the route to  $BrF_n^- + H$  are even larger (Table 8).

## Conclusions

In the present paper, novel stationary points for the  $HBrF_2/HBrF_2^-$  and  $HBrF_4/HBrF_4^-$  systems have been reported. These structures provide a qualitative view of the potential energy hypersurfaces for these species. Perhaps surprisingly, the global minima of the  $HBrF_n/HBrF_n^-$  ( $n = 2, 4$ ) systems are not similar to  $BrF_3$  and  $BrF_5$ , which possess all normal Br–F chemical bonds. The global minima for  $HBrF_n/HBrF_n^-$  are complexes, and some of these equilibrium structures contain hydrogen bonds. Like many interhalogen compounds, most predicted geometries exhibit perpendicular or linear bond angles. This may be rationalized in terms of simple (indeed naive)  $sp^3d$  hybridization or  $sp^3d^3$  hybridization models for the Br atomic orbitals.<sup>24</sup> The valence shell electron pair repulsion also does a good job, certainly for the closed-shell neutrals.

The DFT theoretical predictions of the adiabatic electron affinities ( $EA_{ad}$ ) are 3.69 ( $HBrF_2$ ) and 4.38 eV ( $HBrF_4$ ) with the BHLYP method. These large electron affinities suggest that the anionic species might be observable in the laboratory. No experimental electron affinity values are available so far, but the electron affinity values for the  $HBrF_n$  species are comparable with those for the  $Br_2F_n$ ,  $ClBrF_n$ , and  $BrF_{n+1}$  systems (Table 7).

While the dissociation energies for the complexes to their fragments are small, the first F or H dissociation energies for the  $HBrF_2/HBrF_2^-$  and  $HBrF_4/HBrF_4^-$  global minima are quite

**Table 8.** Dissociation Energies in eV (or in kcal/mol in parentheses) for the  $HBrF_n/HBrF_n^-$  ( $n = 2, 4$ ) Systems<sup>a</sup>

	BHLYP	B3P86	B3LYP	BP86	BLYP
$HBrF_2$ ( <b>2na</b> ) $\rightarrow$ $BrHF$ ( $^2\Sigma^+$ ) + F	2.00 (46.2)	2.72 (62.8)	2.59 (59.8)	3.03 (69.8)	2.94 (67.7)
$HBrF_2$ ( <b>2na</b> ) $\rightarrow$ $BrF_2$ ( $^2A_1$ ) + H	5.16 (119.0)	4.79 (110.5)	4.71 (108.6)	4.33 (99.8)	4.22 (97.4)
$HBrF_4$ ( <b>4na</b> ) $\rightarrow$ $BrHF_3$ ( $^2A'$ ) + F	1.71 (39.4)	2.33 (53.7)	2.14 (49.3)	2.52 (58.1)	2.35 (54.2)
$HBrF_4$ ( <b>4na</b> ) $\rightarrow$ $BrF_4$ ( $^2A_1$ ) + H	5.50 (126.8)	5.08 (117.1)	5.02 (115.8)	4.59 (105.8)	4.51 (103.9)
$HBrF_2^-$ ( <b>2aa</b> ) $\rightarrow$ $BrHF$ ( $^1\Sigma^+$ ) + F	1.49 (34.4)	2.02 (46.7)	2.03 (46.8)	2.32 (53.6)	2.37 (54.7)
$HBrF_2^-$ ( <b>2aa</b> ) $\rightarrow$ $BrHF$ ( $^2\Sigma^+$ ) + $F^-$	2.75 (63.4)	3.01 (69.5)	2.90 (66.9)	3.10 (71.5)	3.01 (69.4)
$HBrF_2^-$ ( <b>2aa</b> ) $\rightarrow$ $BrF_2^-$ ( $^1\Sigma_u^+$ ) + H	4.06 (93.7)	3.89 (89.7)	3.84 (88.6)	3.68 (84.9)	3.61 (83.3)
$HBrF_2^-$ ( <b>2aa</b> ) $\rightarrow$ $BrF_2$ ( $^2A_1$ ) + $H^-$	8.22 (189.7)	9.01 (207.8)	7.72 (178.0)	7.23 (166.8)	7.22 (166.5)
$HBrF_4^-$ ( <b>4aa</b> ) $\rightarrow$ $BrHF_3^-$ ( $^1A'$ ) + F	0.48 (11.1)	1.24 (28.7)	1.19 (27.5)	1.70 (39.3)	1.68 (38.8)
$HBrF_4^-$ ( <b>4aa</b> ) $\rightarrow$ $BrHF_3$ ( $^2A'$ ) + $F^-$	3.15 (72.7)	3.27 (75.4)	3.18 (73.4)	3.24 (74.6)	3.17 (73.0)
$HBrF_4^-$ ( <b>4aa</b> ) $\rightarrow$ $BrF_4^-$ ( $^1A_1$ ) + H	4.30 (99.1)	4.03 (93.0)	4.02 (92.6)	3.81 (87.8)	3.78 (87.1)
$HBrF_4^-$ ( <b>4aa</b> ) $\rightarrow$ $BrF_4$ ( $^2A_1$ ) + $H^-$	9.26 (213.5)	8.72 (201.0)	8.76 (202.0)	8.14 (187.8)	8.25 (190.2)

<sup>a</sup> Not corrected with ZPVE.

large. The first H atom dissociation energies are even larger than the first F atom dissociation energies. For the anions, the dissociation pathways to release an F<sup>-</sup> (or an H<sup>-</sup>) anion have higher barriers than the pathways to release a neutral F (or H) atom.

The primary result of this research is that hypervalency is avoided for BrF<sub>2</sub>H and BrF<sub>4</sub>H. The complexes BrF<sup>•••</sup>HF and BrF<sub>3</sub><sup>•••</sup>HF are the true global minima. In comparison with the hypervalent BrF<sub>3</sub> and BrF<sub>5</sub> molecules, the problem is clear. The energetic drive toward HF complexes arises from the fact that the HF dissociation energy (135 kcal/mol)<sup>26</sup> is so much greater than that for F<sub>2</sub> (37 kcal/mol).<sup>26</sup> From similar arguments, we anticipate that the global minima of PF<sub>4</sub>H, SF<sub>3</sub>H, SF<sub>5</sub>H, ClF<sub>2</sub>H, ClF<sub>4</sub>H, AsF<sub>4</sub>H, SeF<sub>3</sub>H, and SeF<sub>5</sub>H will all be complexes of HF. Finally, it should be noted that many interhalogen molecules are “hermaphroditic”, to use the description of Liebman et al.<sup>27</sup>

(25) Linstrom, P. J., Mallard, W. G., Eds., *NIST Chemistry WebBook, NIST Standard Reference Database*, Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 2003 (<http://webbook.nist.gov>).

That is, these interhalogens form isolable salts with cations and anions of the same formula, in the current case BrF<sub>4</sub> (+ or -). Thus, it would be of interest to consider analogous cationic systems such as BrF<sub>2</sub><sup>+</sup> and HBrF<sub>2</sub><sup>+</sup> in the future.

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**Supporting Information Available:** The vibrational frequencies and infrared intensities for the different global minima. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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