

Bromine Halides: The Neutral Molecules BrClF_n (n = 1–5) and Their Anions — Structures, Energetics, and Electron Affinities

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Abstract: Density functional methods were used for predictions of the structures and energetics of molecules and anions in the series BrClF_n (n = 1–5). Very little is known from experiment about these potentially important interhalogen molecules. Energy minima were found for all neutral molecules with the exception of BrClF₅. However, the dissociation limits for ClF elimination from the BrClF₃ (B3LYP and B3LYP only) and BrClF₄ (all methods) molecules lie below the energy of the respective ground states. All the BrClF_n anions are bound with respect to the corresponding neutrals; energy minima were found for anions up to BrClF₅[−]. Structures of isomers with the chlorine atom in the central position were also optimized. However, these local minima lie substantially above the bromine-centered structures, and the energy gap between isomers grows with n. For the neutral molecules two paths of dissociation were found to possess the lowest energies, i.e., chlorine atom and ClF elimination. The latter channel becomes predominant at n > 1. For the anions the lowest energy dissociation pathways are Cl[−] or Cl elimination, but for n = 3, 5, ClF elimination becomes predominant. The adiabatic electron affinities, the vertical electron affinities of the BrClF_n molecules, and the vertical detachment energies of the BrClF_n[−] anions were predicted in this work. The adiabatic electron affinities of the closed-shell BrClF_n molecules significantly exceed those of the corresponding BrF_n species, while for molecules with an odd number of electrons they are similar or slightly lower than electron affinities in the BrF_n series. Many new experiments are suggested by this researcher, in light of the large predicted electron affinities and the fact that none of these has been measured in the laboratory.

Introduction

Hypervalent interhalogen molecules have attracted the attention of chemists due to interesting aspects of their bonding and their importance as highly oxidizing compounds.^{1–12} Theoretical studies of these molecules have been devoted mainly to the binary compounds of chlorine and fluorine. Much less is known about the interhalogen molecules containing bromine, although these species are of current interest due to their possible roles in atmospheric chemistry.¹³ The dipole moments of the diatomic molecules BrF, BrCl, and BrI have been predicted by MBPT methods (to the fourth order) by Kucharski, Noga, and Bartlett⁷ and by Sadlej.¹¹ And in the recent work of Pak, Xie, Van Huis,

and one of us¹⁴ the structures of the BrF_n (n = 1–6) species were optimized and their electron affinities (EA) were predicted by DFT methods. To the best of our knowledge, no theoretical studies of molecules with ternary combinations of halogen atoms have been reported.

The importance of electron correlation in these molecules for the accurate prediction of their properties (especially of electron affinities) is well-known. However, highly reliable convergent quantum mechanical methods can hardly be applied to the interhalogen molecules with more than three atoms within the current state of the computational resources. The development of methods based on density functional theory (DFT) in recent years has allowed these methods to be applied to interhalogen molecules containing up to eight halogen atoms in ClF_n¹² and BrF_n¹⁴ (n = 1–7). It was shown in these studies that DFT methods appear to give reliable predictions of the structures and energetics of interhalogen compounds. The aim of the present work was the prediction of the structures of the ternary interhalogen molecules BrClF_n (n = 1–5) and their anions and the theoretical estimation of the electron affinities of the neutral molecules.

Theoretical Methods

Four DFT or hybrid HF/DFT methods were used in this work: (1) Becke's 1988 exchange functional (B)¹⁵ with the Lee, Yang, and Parr (LYP) correlation functional¹⁶ (this method is usually designated as

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BLYP); (2) the same Becke exchange functional with the Perdew correlation functional (BP86);¹⁷ (3) Becke's half-and-half exchange functional (BHLYP)¹⁸ with the LYP correlation functional (BHLYP); and (4) Becke's three-parameter exchange functional¹⁹ with the LYP correlation functional (B3LYP). All these methods were used as realized in the GAUSSIAN 94 program.²⁰

Our DZP²⁺ basis set for fluorine was comprised of the standard Huzinaga–Dunning²¹ double- ζ set with one set of d polarization functions [$\alpha_d(\text{F}) = 1.00$] as well as a set of diffuse s [$\alpha_s(\text{F}) = 0.1049$] and p [$\alpha_p(\text{F}) = 0.0826$] functions (10s6p1d/5s3p1d). The contraction scheme for chlorine is (12s8p1d/7s5p1d) and the DZP²⁺ basis set was constructed by using the Huzinaga–Dunning–Hay standard double- ζ sp set²² with polarization d functions [$\alpha_d(\text{Cl}) = 0.75$] and augmented with s and p diffuse functions [$\alpha_s(\text{Cl}) = 0.05048$ and $\alpha_p(\text{Cl}) = 0.05087$]. For bromine the Ahlrichs' double- ζ spd basis set²² with the addition of one set of d-like polarization functions [$\alpha_d(\text{Br}) = 0.389$] and diffuse functions [$\alpha_s(\text{Br}) = 0.0469096$, $\alpha_p(\text{Br}) = 0.0465342$] was used. The contraction scheme for this basis is (15s12p6d/9s7p3d). Pure angular momentum d functions were used throughout. Vibrational frequencies were evaluated for every stationary point found.

The electron affinities are evaluated 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

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

and the vertical detachment energies by

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

One of the reasons for using DFT methods for the prediction of the thermochemical parameters of the open-shell systems is the comparatively low-spin contamination for these methods within the unrestricted spin formalism. The typical single-determinant expectation value of the S^2 operator for doublets in the pure DFT methods (in this work BP86 and BLYP) is 0.752. The degree of contamination is slightly higher for the hybrid methods (B3LYP and especially BHLYP) but it does not exceed 0.76, with one exception (BHLYP for BrClF where it is 0.775).

Results and Discussion

To ascertain the reliability of DFT methods in the prediction of the electron affinities of the ternary interhalogen molecules we predicted these parameters for the constituent F, Cl, and Br atoms and compared them with experiment (Table 1). The different methods employed give acceptable agreement with the experimental electron affinities of the halogen atoms with a few exceptions. However, different methods appeared to give the best prediction for each atom of the series. Thus, for fluorine

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Table 1. The Electron Affinities of F, Cl, and Br in eV (kcal/mol in parentheses) Predicted by Four DFT Methods with the DZP²⁺ Basis Set

method	F	Cl	Br
BHLYP	2.94 (67.8)	3.50 (80.8)	3.41 (78.7)
B3LYP	3.54 (81.7)	3.74 (86.3)	3.60 (83.1)
BP86	3.76 (86.8)	3.84 (88.6)	3.68 (85.0)
BLYP	3.67 (84.8)	3.63 (83.8)	3.46 (79.9)
exptl	3.401 (78.4)	3.613 (83.3) ^a	3.364 (77.6) ^b

^a Reference 23. ^b Reference 24.

Table 2. Predicted Bond Lengths (Å), Vibrational Frequencies (cm⁻¹), Dipole Moments (D), and Dissociation Energies (eV) of BrCl in Comparison with Experiment

method	r_e	ω_e	μ	D_0^0 ^a
BHLYP	2.166	439	0.635	1.64
B3LYP	2.197	411	0.628	1.98
BP86	2.202	403	0.594	2.35
BLYP	2.230	383	0.628	2.16
exptl	2.136 ^b	444 ^b	0.5185(5) ^c	2.23(3) ^b

^a Total energy difference with ZPVE corrections. ^b Reference 22. ^c Reference 25.

the B3LYP result is closest to experiment and that for BHLYP is worst. However, the latter method gave good predictions for Cl and Br. The smallest overall mean error was produced by BLYP. The B3LYP method was also found¹² to be the best in the prediction of the experimental electron affinity of ClF.

A. BrCl. The BrCl molecule in its ground $^1\Sigma^+$ state is the only molecule of the series studied that has been experimentally characterized. The predicted properties of this molecule are compared with experiment in Table 2. As was the case for BrF,¹⁴ all DFT methods give longer bond distances than experiment²³ (2.136 Å). The BHLYP optimized distance is the shortest and is closest to the experimental value (Table 2, **1a**). The harmonic vibrational frequency is also reproduced by the BHLYP method with the highest accuracy. However, this method gives the worst predictions for the dipole moment and dissociation energy. The best reproduction of the dipole moments is achieved with the BP86. The value obtained in this method (0.594 D) is only slightly inferior to the 0.564 D predicted by the MP4 method.⁷

The dissociation energy is also better reproduced by pure DFT methods, i.e., better by BP86 and BLYP than by BHLYP. The BLYP method gives a D_0^0 value with an error of 1.6 kcal/mol error, which is considered to be good for thermochemical predictions. Poor performance in the reproduction of the dissociation energy is demonstrated by BHLYP. Taking into account that the best estimates of known thermochemical parameters of the compounds relevant to our studies are obtained from the BLYP method, we might conclude that the most reliable results in the prediction of electron affinities are expected from this method. Note also that the BLYP method with the DZP²⁺ basis set gives the best estimate of electron affinity of ClF,¹² the only EA known experimentally among the diatomic interhalogen molecules. This method also appeared to be the best in the predictions of electron affinities of diatomic and triatomic first-row molecules²⁷ and medium-ring compounds.²⁸ However, BLYP is not so reliable for the description

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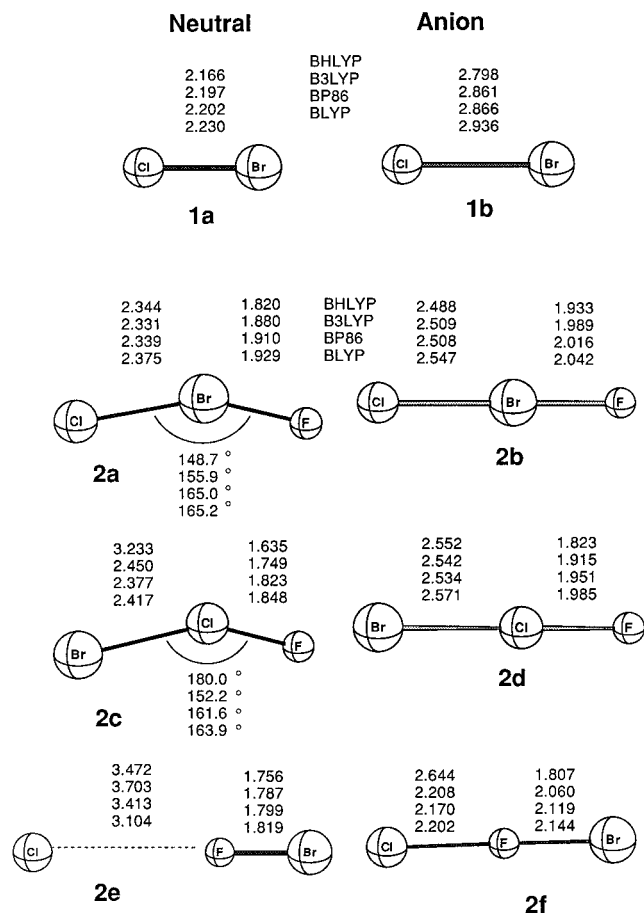


Figure 1. The molecular geometries of the ground states of BrCl ($^1\Sigma^+$, **1a**), BrCl^- ($^2\Sigma^+$, **1b**), BrClF ($^2A'$, **2a**), BrClF^- ($^1\Sigma^+$, **2b**), and their isomers (**2c**, **2d**, **2e**, and **2f**). Bond lengths in Å.

of molecular geometries, and in the previous work¹⁴ on the electron affinities of simpler interhalogen molecules the BHLYP predictions were recommended as most reliable. This conclusion was based on the best reproduction of the molecular geometries of the experimentally characterized interhalogen compounds. The case of BrCl shows again that the method which is the best in describing molecular geometries may be less suitable for predictions of thermochemical parameters. Thus, henceforth we shall refer to the BHLYP predictions while discussing geometrical parameters and those of the BLYP method for the thermochemical parameters unless otherwise stated.

The predicted bond lengths of the ground $^2\Sigma^+$ state of the BrCl^- anion **1b** are depicted in Figure 1. As in the cases of ClF and BrF molecules the attachment of an electron significantly lengthens the BrCl bond. This lengthening can be rationalized by taking into account the antibonding character of the σ LUMO of the BrCl molecule. The tendency toward the spurious increase of interatomic distance in going from BHLYP to BLYP remains in the anion and the theoretical BrCl distance for the anion changes from 2.798 (BHLYP) to 2.936 Å (BLYP).

The electron affinities of BrCl predicted by our four DFT methods are seen in Table 5. Note that the EA_{ad} and EA_{vert} values for BrCl exceed electron affinities estimated at the corresponding level of theory for both BrF and ClF , despite the fact that the electron affinity of bromine is lower than that of chlorine.

Table 3. Predicted Relative Energies of the Three Isomers of BrClF and Dissociation Energies (kcal/mol) of the Most Stable (bromine-centered) Isomer for Neutral ClBrF

isomer	BHLYP	B3LYP	BP86	BLYP
2a , ClBrF	0	0	0	0
2c , BrClF	6.2	13.7	13.6	13.4
2e , ClFBr	3.4	14.9	27.3	24.2
dissociation channel: $\text{ClBrF} \rightarrow X + Y$				
$\text{BrF} + \text{Cl}$	3.5	14.9	27.1	24.3
$\text{ClF} + \text{Br}$	6.5	18.0	29.8	27.7
$\text{BrCl} + \text{F}$	9.6	27.1	41.4	41.3

Table 4. Predicted Relative Energies of Different Isomers of the BrClF^- Anion and Dissociation Energies (kcal/mol) of the Most Stable (bromine-centered) Isomer of the BrClF^- Anion

isomer	BHLYP	B3LYP	BP86	BLYP
2b , ClBrF^-	0	0	0	0
2d , BrClF^-	16.0	13.4	11.8	11.6
2f , ClFBr^-	36.8	30.0	25.8	23.6
dissociation channel: $\text{ClBrF}^- \rightarrow X + Y$				
$\text{BrF} + \text{Cl}^-$	35.3	39.9	44.8	43.1
$\text{ClF} + \text{Br}^-$	40.4	46.2	51.0	50.3
$\text{BrCl} + \text{F}^-$	54.4	56.7	60.9	58.4
$\text{BrF}^- + \text{Cl}$	55.3	61.5	69.1	64.3
$\text{ClF}^- + \text{Br}$	56.0	61.1	68.2	63.2
$\text{BrCl}^- + \text{F}$	51.9	65.6	76.0	73.5

Table 5. Adiabatic (EA_{ad}) and Vertical Electron Affinities (EA_{vert}) of Bromine-Centered BrClF_n Molecules and Vertical Detachment Energies (VDE) of the Anionic Species (eV, kcal/mol in parentheses) Predicted by Four DFT Methods with the DZP++ Basis Set

compd	method	EA_{ad}	EA_{vert}	VDE
BrCl	BHLYP	3.05 (70.3)	1.49 (34.3)	4.54 (104.8)
	B3LYP	3.16 (72.8)	1.73 (40.0)	4.51 (104.0)
	BP86	3.11 (71.7)	1.78 (41.1)	4.38 (101.1)
	BLYP	3.02 (69.7)	1.70 (39.1)	4.26 (98.3)
BrClF	BHLYP	4.88 (112.5)	3.96 (91.3)	5.23 (120.7)
	B3LYP	4.83 (111.3)	4.20 (96.9)	5.06 (116.8)
	BP86	4.61 (106.2)	4.26 (98.3)	4.79 (110.4)
BrClF_2	BHLYP	4.44 (102.5)	4.12 (95.1)	4.61 (106.4)
	B3LYP	4.35 (100.4)	2.66 (61.4)	5.38 (124.0)
	BP86	4.24 (97.7)	3.04 (70.0)	5.17 (119.2)
	BLYP	4.21 (97.1)	3.06 (70.7)	5.10 (117.6)
BrClF_3	BHLYP	5.26 (121.2)	4.44 (102.4)	6.04 (139.2)
	B3LYP	5.62 (129.6)	4.89 (112.7)	5.94 (137.0)
	BP86	5.33 (122.9)	4.92 (113.6)	5.47 (126.2)
	BLYP	5.23 (120.6)	4.95 (114.2)	5.34 (123.3)
BrClF_4	BHLYP	5.25 (121.1)	3.46 (79.8)	7.15 (164.8)
	B3LYP	5.30 (122.3)	3.91 (90.3)	6.49 (149.6)
	BP86	5.05 (116.5)	3.94 (90.9)	5.87 (135.4)
	BLYP	5.12 (118.0)	4.03 (92.9)	5.87 (135.3)
BrClF_5	BHLYP			5.55 (127.9)
	B3LYP			6.36 (146.8)
	BP86			6.43 (148.3)
	BLYP			6.41 (147.7)

B. BrClF . The linear $^2\Pi$ state of the BrClF molecule is subject to the Renner–Teller effect, and the ground state of the molecule is a bent $^2A'$ state (**2a**). The search for other local minima on the potential energy surface was undertaken for three different arrangements of halogen atoms. The structure with the central chlorine atom (**2c**) gives a local minimum that is 13.4 kcal/mol higher in energy than the global minimum (Table 3). The structure with the ClFBr arrangement of the three atoms tends to dissociate to $\text{Cl} + \text{FBr}$. A very loosely bound structure with the $\text{Cl}-\text{F}$ distances in the range 3.104–3.703 Å (**2e**) was located with the DFT method employed, but its dissociation energy to Cl and BrF does not exceed 0.15 kcal/mol and it is

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of little interest for the present study. Thus, only two stable structures were found for the neutral molecule. Both structures **2a** and **2c** lie below the dissociation limits (Table 3) and therefore may be considered possible. The dissociation energy toward BrF + Cl for the second isomer is 10.9 kcal/mol (BLYP). But at B3LYP this dissociation energy is reduced to 1.2 kcal/mol, and it becomes negative (−2.7 kcal/mol) at the BHLYP level (Table 3). This substantial discrepancy in the prediction of the relative stability of isomers and dissociation energies may be traced throughout this work. The BHLYP method (as in the case of diatomic BrCl) systematically underestimates both of these dissociation energies, while the B3LYP results are in a median position between the BHLYP and pure DFT values, the latter (BP86 and BLYP) being very close to each other.

The trend of the equilibrium bond length changes on going from BHLYP to BLYP for this molecule is the same as in the diatomic BrCl. The ClBrF bond angle increases along with the bond length in going from BHLYP to BLYP.

The attachment of an electron to the ClBrF molecule results in the linear ¹Σ⁺ ground state. Indeed, linear anion structures were found for all three arrangements of halogen atoms (**2b**, **2d**, and **2f**). As might be expected the most stable structure is ClBrF[−], followed by BrClF[−] and ClFBr[−] (Table 4). All three anion isomers lie below the dissociation limits. Thus, despite the fact that the trihalogen anion structures are more elongated than those for the analogous neutrals (both bond distances are longer by 0.1–0.15 Å), the anion dissociation energies are surprisingly larger than those for the analogous neutrals.

Table 5 contains the electron affinities predicted for the most stable bromine-centered isomer of ClBrF. The total energies of the most stable isomers for both the neutral and the anion were used in Table 5. The order of values of EA_{ad} obtained with different DFT methods coincides with that reported earlier for BrF₂;¹⁴ the ClBrF EA's decrease in going from BHLYP to BLYP, exceeding the corresponding BrF₂ values by 0.1–0.15 eV. All EA_{vert} values are likewise greater than their BrF₂ analogues by 0.12–0.14 eV. The VDE values for BrClF obtained by the BHLYP and B3LYP methods are significantly smaller than those for BrF₂, while the BP86 and BLYP results are nearly equal to the corresponding values predicted for BrF₂¹⁴ (Table 5). The predicted electron affinities of the chlorine-centered isomer BrClF (Table 6) are comparable to those of the more stable bromine-centered structure.

C. BrClF₂. The equilibrium structures for both the neutral and the anion have C_{2v} symmetry. The BrClF₂ molecule (**3a**) in its ¹A₁ ground state is characterized by longer BrF bonds (1.834 Å) than those of its BrF₃ cousin (1.808 Å).¹⁴ The BrCl bond length (2.156 Å) is shorter than that for the BrClF radical and is nearly equal to that of the BrCl molecule.

Of the different plausible dissociation channels for this ¹A₁ state the lowest lying is BrF + ClF (Table 7). The latter dissociation energy is 12.1 kcal/mol (BLYP) above **3a** but is reduced in going from pure to hybrid DFT methods. As usual the BHLYP method underestimates the dissociation energy and neutral BrClF₂ appears to be dissociative at this level of theory (Table 7). The second lowest energy channel is BrF₂ + Cl (29.7 kcal/mol above BrClF₂), followed by BrCl + F₂ (42.3 kcal/mol), Br + ClF₂ (45.6 kcal/mol), and F + BrClF (50.5 kcal/mol).

As was the case with BrCl, the structure of the anionic counterpart of BrClF₂ (**3b**) is characterized by a significant lengthening of the BrCl bond (2.788 Å) relative to the neutral molecule (2.156 Å, **3a**). All methods uniformly predict the bond distances of both neutral and anionic BrClF₂ to be slightly (by

Table 6. Adiabatic (EA_{ad}) and Vertical Electron Affinities (EA_{vert}) of Chlorine-Centered BrClF_n Molecules and Vertical Detachment Energies (VDE) of the Anionic Species (eV, kcal/mol in parentheses) Predicted by Four DFT Methods with the DZP⁺⁺ Basis Set

compd	method	EA _{ad}	EA _{vert}	VDE
BrClF	BHLYP	4.46 (102.7)	3.50 (80.7)	4.90 (112.9)
	B3LYP	4.84 (111.6)	4.18 (96.4)	5.10 (117.5)
	BP86	4.68 (108.0)	4.29 (98.8)	4.85 (111.8)
	BLYP	4.52 (104.3)	4.20 (96.8)	4.68 (107.9)
BrClF ₂	BHLYP	4.84 (111.8)	3.23 (74.5)	6.36 (146.7)
	B3LYP	4.83 (111.4)	3.48 (80.1)	5.87 (135.4)
	BP86	4.63 (106.8)	3.52 (81.2)	6.55 (151.0)
	BLYP	4.59 (105.8)	3.52 (81.2)	5.35 (123.5)
BrClF ₃	BHLYP	4.66 (107.6)	4.07 (93.8)	5.61 (129.3)
	B3LYP	5.33 (123.0)	4.65 (107.3)	5.94 (137.0)
	BP86	5.47 (126.1)	5.20 (119.8)	5.62 (129.5)
	BLYP	5.40 (124.4)	5.18 (119.5)	5.54 (127.8)
BrClF ₄	BHLYP	6.22 (143.6)	4.63 (106.9)	8.09 (186.7)
	B3LYP	6.12 (141.0)	4.90 (113.0)	7.13 (164.5)
	BP86	5.80 (133.7)	4.90 (113.1)	6.36 (146.6)
	BLYP	5.82 (134.3)	5.06 (116.6)	6.33 (146.0)
BrClF ₅	BHLYP			5.55 (127.9)
	B3LYP			6.17 (142.2)
	BP86			6.26 (144.4)
	BLYP			6.20 (143.0)

ca. 0.01 Å) longer than those for BrCl. The same effect will be seen for BrClF₄. This suggests that the addition of an even number of fluorines has a small effect on the bonding in the BrCl moiety, in contrast to the addition of odd numbers of fluorine atoms.

The BrClF_n anions have more distinct binary channels of dissociation than the analogous neutrals; the negative charge may reside on either of the two fragments. Pak et al.¹⁴ have shown that in the case of BrF_n[−] (n = 1–4), anions with an odd number of electrons tend to dissociate to BrF_{n−1}[−] + F, while the channel BrF_{n−1} + F[−] is preferable for anions with an even number of electrons. However, this tendency disappears for n > 4 for the binary bromine fluorides. But in BrF₃[−] the dissociation energy of the first channel is still substantially lower than that of the second. Substitution of one fluorine by chlorine significantly increases the number of plausible channels of dissociation. We found that for BrClF₂[−] the lowest energy channel, i.e., Cl + BrF₂[−], is predicted to have a dissociation energy of 26.6 kcal/mol. This is in accord with the above rule. Two other channels with the elimination of a neutral halogen atom are the following: Br + ClF₂[−] (36.2 kcal/mol) and F + BrClF[−] (45.2 kcal/mol). The referee has noted that dissociation of **3b** to Br + ClF₂[−] may not be kinetically realistic. As for BrClF[−], in the case of anionic BrClF₂ different methods show more uniform results in the prediction of dissociation energies than do those for neutral molecules.

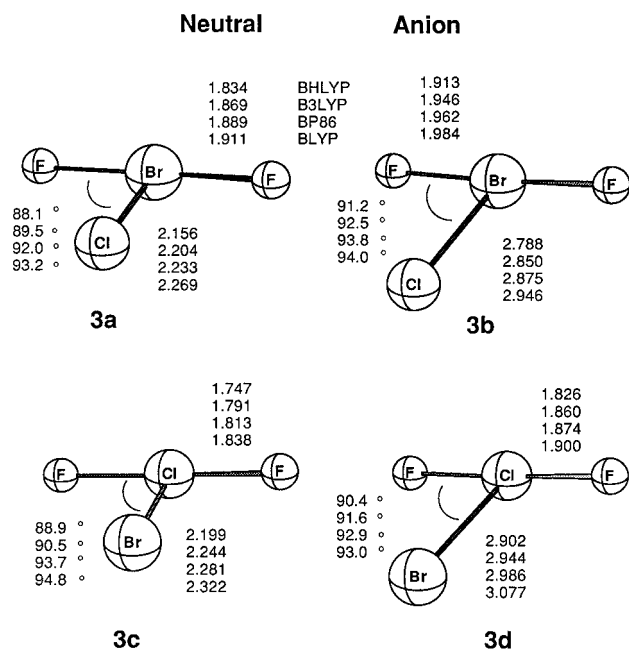
Isomers (both for neutral and anion) which may be derived from the attachment of atomic bromine to the ClF₂ moiety were found as local minima on the PES. They are 26.7 (neutral, **3c**) and 18.0 kcal/mol (anion, Figure 2, **3d**) above the corresponding global minima (Table 8). The neutral isomer is prone to dissociation since the lowest energy dissociation limit is below this minimum. However, dissociation to ClF + BrF may require a substantial barrier and the least-motion dissociation pathway (Br + ClF₂) has a higher energy (45.6 kcal/mol). The anionic chlorine-centered isomer (**3d**) may be favorable, since the lowest energy dissociation limit lies 8.6 kcal/mol higher.

The predicted adiabatic electron affinities of BrClF₂ are higher than the corresponding values for BrF₃ by 0.5–0.6 eV. Similar relationships are observed also for EA_{vert} and VDE (Table 5). The electron affinities of the chlorine-centered isomer, in

Table 7. Dissociation Energies (kcal/mol) of the Lowest Energy Dissociation Channels of Neutral and Anionic Species of BrClF_n

Bromine Centered Neutrals BrClF_n												
<i>n</i>	$\text{Cl} + \text{BrF}_n$				$\text{ClF} + \text{BrF}_{n-1}$							
	BHLYP	B3LYP	BP86	BLYP	BHLYP	B3LYP	BP86	BLYP	BHLYP	B3LYP	BP86	BLYP
1	3.5	14.9	27.1	24.3	6.5	18.0	29.8	27.7				
2	24.0	28.5	34.1	29.7	-2.8	5.2	14.7	12.1				
3	1.3	5.2	18.5	15.8	-1.7	-1.8	8.9	5.8				
4	12.5	17.1	23.0	18.1	-19.8	-11.2	-0.2	-3.9				

Bromine Centered Anions BrClF_n^-												
<i>n</i>	$\text{Cl}^- + \text{BrF}_n$				$\text{Cl} + \text{BrF}_n^-$				$\text{ClF} + \text{BrF}_{n-1}^-$			
	BHLYP	B3LYP	BP86	BLYP	BHLYP	B3LYP	BP86	BLYP	BHLYP	B3LYP	BP86	BLYP
1	35.3	39.9	44.8	43.1	55.3	61.5	69.1	64.3	40.4	46.2	51.0	50.3
2	30.8	43.8	43.2	43.1	14.2	21.5	28.8	26.6	36.8	42.2	48.1	46.7
3	41.7	48.5	52.8	52.6	35.5	45.2	55.1	49.6	9.5	19.2	28.7	26.2
4	52.8	53.1	50.9	52.3	4.9	10.8	18.3	16.0	14.3	21.4	30.0	27.3
5	33.4	46.6	53.7	55.5	16.5	29.7	42.7	36.8	-16.9	-4.3	9.2	5.5

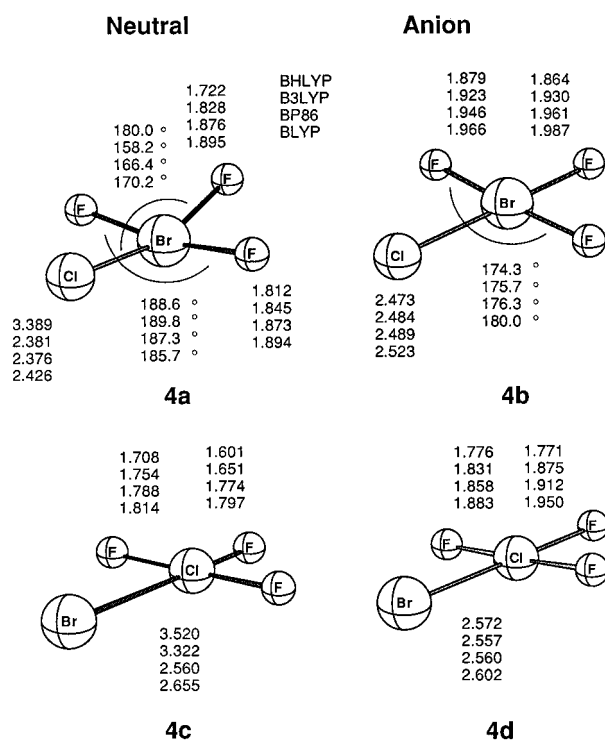
**Figure 2.** The molecular geometries of the ground states of BrClF_2 ($^1A'$, **3a**), BrClF_2^- ($^2A'$, **3b**), and chlorine-centered isomers **3c** and **3d**. Bond lengths in Å.**Table 8.** Energy Differences (kcal/mol) between the Bromine-Centered and Chlorine-Centered Isomers of the BrClF_n Molecules and Anions^a

<i>n</i>	neutral				anion			
	BHLYP	B3LYP	BP86	BLYP	BHLYP	B3LYP	BP86	BLYP
1	6.2	13.7	13.6	13.4	16.0	13.4	11.8	11.6
2	30.9	28.9	27.1	26.7	19.5	19.2	18.1	18.0
3	33.0	34.8	40.6	39.8	46.7	41.4	37.4	35.9
4	70.2	65.3	61.8	60.4	47.8	46.6	44.6	44.0
5					84.7	76.4	69.6	69.0

^a The bromine-centered species are uniformly lower in energy.

contrast to the BrClF system, do not differ much from those of the most stable bromine-centered isomer.

D. BrClF_3 . The prototype BrF_4 molecule in its ground 2A_1 state has C_{4v} symmetry. Chlorine substitution lowers the equilibrium symmetry, to C_s . The geometrical parameters of the BrClF_3 ground state ($^2A'$) are depicted in Figure 3, structure **4a**. There is a discrepancy between predictions of the neutral BrClF_3 structure made by BHLYP on one hand and the three other DFT methods on the other. BHLYP predicts a loose

**Figure 3.** The molecular geometries of the ground states of BrClF_3 ($^2A'$, **4a**), BrClF_3^- ($^1A'$, **4b**), and their chlorine-centered isomers **4c** and **4d**. Bond lengths in Å.

complex between Cl and BrF_3 with the BrCl bond distance of 3.389 Å. This equilibrium bond length obtained by three other methods is around 2.4 Å. In this case only it would appear that the BHLYP structure may be less reliable than those predicted by the other three methods. It appears that BHLYP's failure to predict a substantial dissociation energy results in qualitatively incorrect geometrical structure. However, this hypothesis should be tested with convergent quantum mechanical methods, i.e., coupled cluster theory.

Like the BrClF_2 molecule, BrClF_3 has its lowest energy dissociation channel for ClF elimination (5.8 kcal/mol). However, both hybrid DFT methods predict this molecule to lie above the ClF elimination product (Table 7). Provided that the pure DFT methods give more reliable thermochemical predictions, we may conclude that the neutral BrClF_3 molecule is thermodynamically stable. The least-motion pathway ($\text{Cl} + \text{BrF}_3$) has a substantial dissociation energy, far above zero even with the hybrid DFT methods.

The discrepancy between two groups of DFT methods in the prediction of the structure of the neutral isomer with the chlorine atom in the central position **4c** is similar to that for bromine-centered isomer (**4a**). However, in the case for structure **4c** not only the BHLYP method but also the B3LYP method predict loose BrCl bonding. On the contrary, pure DFT methods show only small elongation of the BrCl bond in going from **4a** to **4c**.

The bromine-centered BrClF_3^- anion (**4b**) is stable toward dissociation. The two channels for chlorine elimination have similar dissociation energies [$\text{Cl} + \text{BrF}_3^-$ (49.6 kcal/mol) and $\text{Cl}^- + \text{BrF}_3$ (52.6 kcal/mol)]. These two channels had the lowest energy in the previously discussed systems. But for the BrClF_3^- anion, the ClF elimination channel with the 26.2 kcal/mol dissociation energy becomes the most accessible (Table 7).

The chlorine-centered isomer of BrClF_3^- is predicted 35.9 kcal/mol above **4b** and lies above the limit for $\text{ClF} + \text{BrF}_2^-$ dissociation. But this isomer does lie below the least-motion dissociation pathway limit, i.e., $\text{Br}^- + \text{ClF}_3$.

Despite the significant deviation of the BHLYP equilibrium geometrical parameters, the adiabatic electron affinity of BrClF_3 is fortuitously close to those obtained by BP86 and BLYP (Table 4). But the B3LYP EA_{ad} value is substantially greater than that obtained with the three other methods. All these discrepancies indicate that BrClF_3 is a challenging target for DFT methods. In general the predicted adiabatic electron affinity of BrClF_3 is the greatest in the series, presumably due to instability of the neutral system.

E. BrClF_4 . Addition of a chlorine atom to BrF_4 forms a BrClF_4 molecule which is found to be a minimum on its PES with all methods employed. The analogous interhalogen molecules ClF_5 and BrF_5 are characterized experimentally, but there is no experimental evidence to date for the existence of the BrClF_4 molecule. Optimized geometrical parameters for the ground ${}^2\text{A}_1$ state of this molecule are shown in Figure 4, structure **5a**. As with BrClF_2 , the BrCl bond lengths, obtained with various DFT methods for BrClF_4 , are very similar to those of the BrCl molecule, although a tendency of a slight elongation of this distance on going from BrCl to BrClF_4 can be observed.

Similar trends may be found in the anionic $\text{BrCl}^- \rightarrow \text{BrClF}_2^- \rightarrow \text{BrClF}_4^-$ series. Attachment of an electron increases the BrCl bond length by ca. 0.65 Å for all molecule of the series (**1b–3b–5b**) with a much smaller effect on the BrF bond lengths (ca. 0.1 Å).

As with the previous closed-shell molecule BrClF_2 , the lowest energy channel for dissociation of BrClF_4 is that of ClF elimination. In contrast to BrClF_2 where the ground-state minimum was stable (with the exception of BHLYP), the neutral bromine-centered BrClF_4 (**5a**) appears to be thermodynamically unstable with respect to this dissociation at all theoretical levels (Table 7). However, the barrier for this dissociation may be substantial, and **5a** is stable with respect to the least-motion dissociation pathway involving chlorine atom elimination (Table 7). Other channels for dissociation have much higher energies: $\text{F}_2 + \text{BrClF}_2$ (33.1 kcal/mol) and $\text{F} + \text{BrClF}_3$ (43.1 kcal/mol).

Despite the location of an electron on an orbital with antibonding character and the looseness of the BrCl bond in the BrClF_4^- anion, this anion is more favorable than the corresponding neutral molecule. The lowest energy channel for dissociation to $\text{Cl}^- + \text{BrF}_4$ is 16.0 kcal/mol above the **5b** minimum (Table 7).

Local minima for the neutral and anionic isomers with the central chlorine atoms were also found (**5c** and **5d**). However, they are 60.4 (neutral) and 44.0 kcal/mol (anion) above the corresponding lower energy isomers.

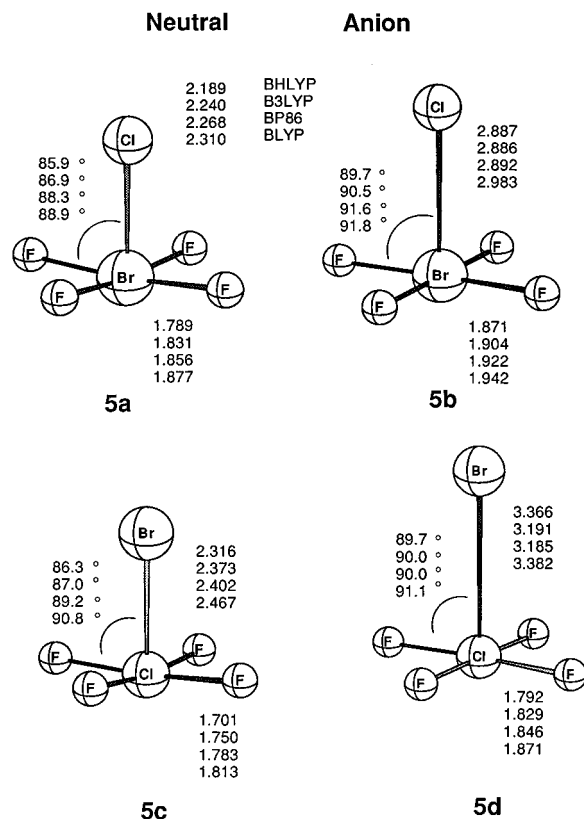


Figure 4. The molecular geometries of the ground states of BrClF_4 (${}^1\text{A}_1$, **5a**), BrClF_4^- (${}^2\text{A}_1$, **5b**), and their chlorine-centered isomers **5c** and **5d**. Bond lengths in Å.

F. BrClF_5 . All attempts to locate a minimum on the PES of the neutral BrClF_5 radical failed. One might expect this in terms of the tendency of the dissociation energy change with number of fluorine atoms (n) in the BrClF_n neutrals (Table 5). The energy of the least-motion dissociation channel $\text{Cl} + \text{BrF}_n$ steadily decreases in each series, including both the closed-shell ($n = 2, 4$) and open-shell ($n = 1, 3$) systems (Table 7). Thus we may expect that for $n = 5$ not only the dissociation energy for ClF elimination but also the least-motion pathway becomes energetically downhill.

The analogous tendency for anionic species exists but starts from higher dissociation energies compared to the neutrals. The BrClF_5^- anion (**6b**) was found as a minimum on the PES by all DFT methods used. This structure (${}^1\text{A}_1$ in C_{4v} point group) is stable relative to dissociation with neutral chlorine atom elimination, but hybrid DFT methods predict (**6b**) to lie above the dissociation limit for ClF elimination (Table 7). However, more reliable for thermochemical predictions is the BLYP method, with a dissociation energy of 5.5 kcal/mol. Note that the BHLYP optimized geometry differs somewhat from three others, however not so dramatically as discussed above for BrClF_3 . There is also a peculiar difference in the prediction of the BrF bond lengths: hybrid methods predict the equatorial CF bonds to be longer than the axial, while pure DFT methods predict the converse order of BrF bond lengths. Again, convergent quantum mechanical methods [e.g., CCSD(T)] would be required to settle this issue definitely.

The chlorine-centered isomer of the BrClF_5^- anion also exists as a minimum on the PES of the system (**6d**), but it is predicted to lie 60 kcal/mol higher than the bromine-centered isomer (Table 8).

G. General Trends in Energetics and Electron Affinities of BrClF_n ($n = 1-5$) Species. For neutrals with $n = 1-4$,

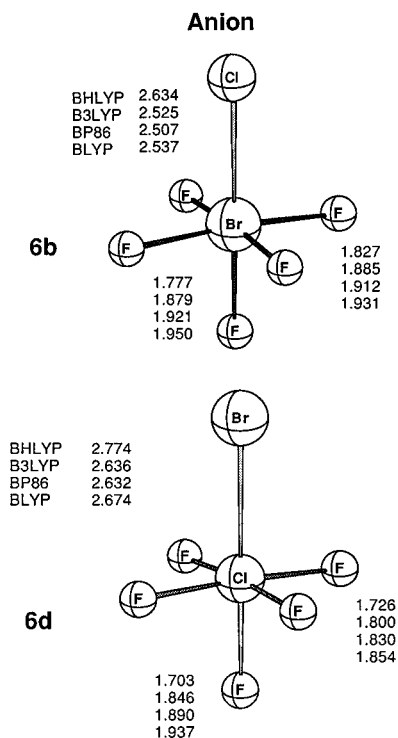


Figure 5. The molecular geometries of the ground states of the BrClF_5^- anion **6b** and its chlorine-centered isomer **6d**. Bond lengths in Å.

minima on potential energy surfaces were found at all levels of theory employed. However, the thermodynamic stabilities decrease with n in this series. For the BrClF_3 molecule, the hybrid DFT methods (BHLYP and B3LYP) predict thermodynamic instability with respect to ClF elimination, while the BrClF_4 molecule appears to be disfavored at all levels of theory employed (Table 7). Least-motion dissociation products, however, still lie above the minima for the bound neutral molecules with n up to 4. The increasing instability with n results in the absence of a substantial energy minimum in the BrClF_5 system. Dissociation energies obtained at different theoretical levels show a steady growth in the order $\text{BHLYP} \rightarrow \text{B3LYP} \rightarrow \text{BLYP} \rightarrow \text{BP86}$ (Table 7). This order coincides with that predicted for the BrCl molecule where comparison with experiment indicates the BLYP method to be the most accurate (Table 2). The apparent reliability of the geometry predictions increases in the nearly inverse order $\text{BLYP} \rightarrow \text{BP86} \rightarrow \text{B3LYP} \rightarrow \text{BHLYP}$. Thus, the B3LYP method taking the median position in both sequences may be regarded as a compromise between the reliabilities of geometry and thermochemical parameter predictions.

All anions BrClF_n^- studied are thermodynamically stable toward dissociation, although the dissociation energies also

decrease with n . The lowest energy dissociation channels for anions with $n = 1, 2$ are $\text{Cl}^- + \text{BrClF}_n$ and $\text{Cl} + \text{BrClF}_n^-$. For the closed-shell BrClF_5^- , dissociation into two closed-shell moieties Cl^- and BrF_5 is preferable. The radical BrClF_2^- tends to dissociate to $\text{Cl} + \text{BrF}_2^-$. The next anion BrClF_3^- breaks this tendency, in that the lowest energy channel appears to be $\text{ClF} + \text{BrF}_2^-$. The radical anion BrClF_4^- again prefers to dissociate with elimination of the neutral chlorine atom, but the next closed-shell anion BrClF_5^- shows preference of ClF elimination over that of Cl^- (Table 7).

For all systems studied with the exclusion of BrClF_5 , local minima corresponding to structures with a central chlorine atom exist. However, some of these (**3d**, **4c**, and **5d**) may be very weakly bound. The gap between bromine- and chlorine-centered isomers grows with n (Table 8). Since dissociation energies decrease in this series (Table 7) the chlorine-centered neutrals with $n > 1$ and anions with $n > 2$ lie energetically above the lowest energy channel, while still being stable relative to the least-motion dissociation channel, and may exist, provided that the barrier for non-least-motion dissociation is substantial (which seems probable).

There are two types of BrCl bonds and correspondingly different changes on going from neutral to anion. Closed-shell neutrals BrClF_n (n even) have comparatively short BrCl bonds (ca. 2.2 Å) and significant lengthening in their anions (2.8–3.0 Å). The radical neutrals have longer BrCl bonds (2.3–2.4 Å) but their changes on going to anions are comparatively small (2.4–2.6 Å).

The trends in electron affinities for the systems studied are also readily divided into two groups, depending on the parity of the number of electrons. For each group there is growth with n of all three types of electron affinity. The adiabatic electron affinity reaches a kind of saturation with $n = 4$, and EA_{ad} for BrClF_3 is even slightly greater than that for BrClF_4 . The vertical electron affinity of BrClF_3 is also the greatest in the series, but the predicted VDE values for BrClF_4^- substantially exceed those of the other anions.

Comparing electron affinities predicted in this study with those reported earlier¹⁴ for BrF_n obtained by the same method/basis set, one notices that for closed-shell neutrals the EA_{ad} of BrClF_n are greater than for the bromine fluorides with the same number of atoms, while there is only a small difference for open-shell neutrals. Thus, the predicted EA_{ad} for BrClF_4 (n even) exceeds the corresponding values of BrF_5 by 0.7–1.0 eV, while BrF_4 and especially BrF_6 (the analogous neutral BrClF_5 is not significantly bound) have the highest values among the bromine halides.

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