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Article

BX_4^- and AlX_4^- Superhalogen Anions (X = F, Cl, Br): An ab Initio Study

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The vertical electron detachment energies (VDEs) of 30 MX_4^- (M = B, Al; X = F, Cl, Br) anions were calculated at the OVGF level with the 6-311+G(3df) basis sets. The largest vertical electron binding energy was found for the AlF_4^- system (9.789 eV). The strong VDE dependence on the symmetry of the species, ligand type, ligand−central atom distance, and bonding/nonbonding/antibonding character of the highest occupied molecular orbital was observed and discussed.

1. Introduction

Superhalogens are molecules with electron affinities (EAs) that are larger than those of the halogen atoms (fluorine 3.40 eV, chlorine 3.62 eV[1]). Such species are of a great importance in chemistry since they can be used for the oxidation of counterpart systems with relatively high ionization potentials (such as O_2, Xe) and allow the synthesis of unusual chemical compounds (e.g., involving nobel gas atoms).[2] In addition, molecules possessing high electron affinities are widely used in the production of organic superconductors.[3]

In 1981, Gutsev and Boldyrev introduced a simple formula for one class of superhalogens, MX_{k+1}, where M is a main group or transition metal atom, X is a halogen atom, and k is the maximal formal valence of the atom M.[4] Since the early 1980s, many other theoretical efforts have been undertaken to estimate the vertical electron detachment energies (VDEs) of various anions having superhalogens as their neutral parents (see refs 5–9 and references cited therein). In 1999, dramatic progress was made in the investigation of superhalogen systems due to a joined theoretical and experimental effort that resulted in an excellent report comprising the first experimental photoelectron spectra of superhalogens (measured by the Wang's group) together with theoretical interpretations provided by Boldyrev and Simons.[10] In particular, the photoelectron spectra of MX_2^- (where M = Li, Na, and X = Cl, Br, I) anions were obtained and assigned on the basis of ab initio outer-valence Green function (OVGF) calculations. Excellent agreement between experimentally and theoretically estimated values of VDEs has been achieved, and all of the anions have proven to be superhalogen-based species since their electron binding energies were found to be greater than 3.62 eV (see ref 10 for details).

Recently, Boldyrev's and Wang's groups studied and described MX_3^- (M = Be, Mg, Ca; X = Cl, Br)[11] and even larger superhalogen species, such as $Na_xCl_{x+1}^-$ ($x = 1-4$).[12] Our group contributed to this field by examining BeX_3^- (X = F, Cl, Br),[13] MgX_3^- and CaX_3^- (X = F, Cl, Br),[14] and NaX_2^- anions (X = F, Cl, Br),[15] including "mixed" (containing various halogen ligands) species, such as $BeFCl_2^-$, $MgClBr_2^-$, $CaFClBr^-$, or $NaFBr^-$. In addition, we performed a theoretical search for anions possessing extremely large electron binding energies, which resulted in finding a polynuclear superhalogen anion $Ta_3F_{16}^-$ whose

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binding energy was estimated to be 12.63 eV.[16] Most recently, we reported our findings for HF_2^-, HCl_2^-, HBr_2^-, and $H_2F_3^-$ and proved that the hydrogen atom may play a central atom role in superhalogen anions.[17]

Exploring various new superhalogen species is primarily focused on studying larger molecular clusters which are capable of forming strongly bound anions. The purpose of these efforts is to provide reliable data and predictions considering the possible use of such compounds as electron acceptors in the production of organic superconductors, as well as the role they can play in synthesis (e.g., in the oxidation of counterpart systems with high ionization potentials).

In the preceding papers, we reported our findings considering unusual geometrical structures of $Mg_2F_5^-$ (VDE = 9.4 eV) in which two central Mg atoms are linked through a symmetrical triangular bridge built of three halogen atoms.[18]

In the course of our studies, we encountered superhalogen anions matching the MX_4^- formula (where M = B, Al; X = F, Cl, Br). In particular, Gutsev and co-workers found that both BF_4^- and AlF_4^- are of T_d symmetry and strongly bind an extra electron (the calculated EAs were 6.75 and 7.93 eV, respectively).[19] It was quite unique (for this kind of species) to explore also the geometrical structure of the corresponding neutral parents; however, Gutsev and co-workers managed to find the neutral BF_4 and AlF_4. As was shown, the BF_4 has a configuration of an adduct type (BF_3*F) while the AlF_4 should rather be considered as a van der Waals complex ($AlF_3 \cdots F$). Determining the geometrical structures of the neutral parent systems allowed also for including the zero-point vibrational energy corrections in the calculated EAs for the superhalogens studied.[19] Although valuable, these earlier studies described in the literature are incomplete since they do not contain any data on "mixed" species, such as $BF_2Cl_2^-$, $BFClBr_2^-$, AlF_3Cl^-, or $AlFBr_3^-$. This lack of data has motivated us to take a closer look at the various superhalogen anions containing B or Al as a central atom and to calculate their vertical electron detachment energies. In this contribution, we present our ab initio results for 30 negatively charged species exhibiting "superhalogen nature" and having B or Al as the metal component (in MX_4^-). We believe that the vertical electron binding energies we provide in this work might be found useful for experimental chemists, especially those who design new materials in which strong electron acceptors are involved.

2. Methods

Since our main goal was to calculate the vertical electron detachment energies for the MX_4^- anions (M = B, Al; X = F, Cl, Br), we limited our geometry optimization calculations to the closed-shell anionic species, for which we also obtained harmonic vibrational frequencies at their minimum energy structures. For this purpose, we applied the second-order Møller−Plesset (MP2) perturbational method with the 6-311+G(d) basis sets.[20,21] Providing reliable vertical electron detachment energies of the MX_4^- anions requires using more accurate treatment; thus, we decided to perform both *direct* and *indirect* calculations of the electron binding energies. A *direct* scheme was based on applying the OVGF method,[22–26] while the latter (*indirect*) approach consisted of subtracting the anion energies from those of the neutral (both calculated at the same level of theory, which was the MP2 level in our case). The OVGF approximation remains valid only for outer-valence ionizations for which the pole strengths (PSs) are greater than 0.80−0.85.[27] For all states studied here, the PSs are sufficiently large to justify the use of the OVGF method (the smallest PS found for the states studied in this work is 0.90).

As far as the basis sets are concerned, we applied the 6-311+G(3df) basis sets[20,21] while estimating vertical electron detachment energies at various levels, since analogous basis sets have been used by others for superhalogen anions and provided an excellent agreement between such calculated and experimentally measured VDEs.[10,12–14]

All calculations were performed with the Gaussian 03 program.[28]

3. Results

3.1. The MP2 Equilibrium Geometries and Vibrational Frequencies. The MP2 minimum energy structures of the superhalogen anions BX_4^- and AlX_4^- (X = F, Cl, Br) are characterized in Tables 1 and 2, where the corresponding harmonic vibrational frequencies are also collected. Since for each negatively charged system studied in this work all of the Hessian matrix eigenvalues were found positive, we are confident that these structures correspond to the minima on the MP2 ground-state anionic potential energy surface.

The MP2 minimum energy structures of the MX_4^- (M = B, Al; X = F, Cl, Br) anions possess T_d (BF_4^-, BCl_4^-, BBr_4^-, AlF_4^-, $AlCl_4^-$, and $AlBr_4^-$), C_{3v} ($BFBr_3^-$, $BClBr_3^-$, BCl_3Br^-, BF_3Br^-, $BFCl_3^-$, BF_3Cl^-, $AlFBr_3^-$, $AlClBr_3^-$, $AlCl_3Br^-$, AlF_3Br^-, $AlFCl_3^-$, and AlF_3Cl^-), C_{2v} ($BF_2Br_2^-$, $BCl_2Br_2^-$,

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Table 1. The MP2 Geometrical Parameters, Corresponding Harmonic Vibrational Frequencies, and the OVGF/6-311+G(3df) VDEs for the BX_4^- (X = F, Cl, Br) Anions Studied in This Work[a]

species and symmetry point group	VDE^{OVGF} 6−311+G(3df)	geometry	frequencies $[cm^{-1}]$
BF_4^-, T_d	8.975	R(B−F) = 1.415	$\nu_1 = 347\ (e),\ \nu_2 = 510\ (f_2)$
		∠(FBF) = 109.47	$\nu_3 = 743\ (a_1),\ \nu_4 = 1059\ (f_2)$
BF_3Cl^-, C_{3v}	6.428	R(B−F) = 1.403	$\nu_1 = 283\ (e),\ \nu_2 = 389\ (a_1)$
		R(B−Cl) = 1.898	$\nu_3 = 468\ (e),\ \nu_4 = 660\ (a_1)$
		∠(FBCl) = 109.47	$\nu_5 = 888\ (a_1),\ \nu_6 = 1077\ (e)$
$BF_2Cl_2^-$, C_{2v}	6.089	R(B−F) = 1.392	$\nu_1 = 226\ (a_1),\ \nu_2 = 265\ (a_2)$
		R(B−Cl) = 1.884	$\nu_3 = 369\ (b_2),\ \nu_4 = 373\ (b_1)$
		∠(FBCl) = 109.47	$\nu_5 = 393\ (a_1),\ \nu_6 = 580\ (a_1),\ \nu_7 = 750\ (b_1),\ \nu_8 = 976\ (a_1),\ \nu_9 = 1094\ (b_2)$
$BFCl_3^-$, C_{3v}	6.076	R(B−F) = 1.384	$\nu_1 = 215\ (e),\ \nu_2 = 306\ (a_1)$
		R(B−Cl) = 1.871	$\nu_3 = 351\ (e),\ \nu_4 = 478\ (a_1)$
		∠(FBCl) = 109.47	$\nu_5 = 741\ (e),\ \nu_6 = 1055\ (a_1)$
BF_3Br^-, C_{3v}	5.729	R(B−F) = 1.398	$\nu_1 = 246\ (e),\ \nu_2 = 277\ (a_1)$
		R(B−Br) = 2.092	$\nu_3 = 465\ (e),\ \nu_4 = 639\ (a_1)$
		∠(FBBr) = 109.47	$\nu_5 = 857\ (a_1),\ \nu_6 = 1088\ (e)$
BCl_4^-, T_d	6.218	R(B−Cl) = 1.860	$\nu_1 = 195\ (e),\ \nu_2 = 286\ (f_2)$
		∠(ClBCl) = 109.47	$\nu_3 = 420\ (a_1),\ \nu_4 = 737\ (f_2)$
BF_2ClBr^-, C_s	5.653	R(B−F) = 1.388	$\nu_1 = 186\ (a'),\ \nu_2 = 241\ (a'')$
		R(B−Cl) = 1.876	$\nu_3 = 281\ (a'),\ \nu_4 = 349\ (a'')$
		R(B−Br) = 2.077	$\nu_5 = 386\ (a'),\ \nu_6 = 564\ (a')$
		∠(FBCl) = 109.47	$\nu_7 = 709\ (a'),\ \nu_8 = 976\ (a')$
		∠(FBBr) = 109.47	$\nu_9 = 1104\ (a'')$
$BFCl_2Br^-$, C_s	5.712	R(B−F) = 1.380	$\nu_1 = 178\ (a''),\ \nu_2 = 190\ (a')$
		R(B−Cl) = 1.864	$\nu_3 = 264\ (a'),\ \nu_4 = 296\ (a')$
		R(B−Br) = 2.063	$\nu_5 = 349\ (a''),\ \nu_6 = 451\ (a')$
		∠(ClBBr) = 109.47	$\nu_7 = 680\ (a'),\ \nu_8 = 746\ (a'')$
		∠(FBBr) = 109.47	$\nu_9 = 1061\ (a')$
BCl_3Br^-, C_{3v}	5.827	R(B−Cl) = 1.854	$\nu_1 = 170\ (e),\ \nu_2 = 224\ (a_1)$
		R(B−Br) = 2.050	$\nu_3 = 269\ (e),\ \nu_4 = 387\ (a_1)$
		∠(ClBBr)=109.47	$\nu_5 = 663\ (a_1),\ \nu_6 = 742\ (e)$
$BF_2Br_2^-$, C_{2v}	5.456	R(B−F) = 1.384	$\nu_1 = 142\ (a_1),\ \nu_2 = 227\ (a_2)$
		R(B−Br) = 2.069	$\nu_3 = 279\ (b_2),\ \nu_4 = 294\ (a_1)$
		∠(FBBr) = 109.47	$\nu_5 = 316\ (b_1),\ \nu_6 = 549\ (a_1),\ \nu_7 = 661\ (b_2),\ \nu_8 = 972\ (a_1),\ \nu_9 = 1113\ (b_1)$
$BFClBr_2^-$, C_s	5.545	R(B−F) = 1.376	$\nu_1 = 141\ (a'),\ \nu_2 = 173\ (a'')$
		R(B−Cl) = 1.858	$\nu_3 = 236\ (a'),\ \nu_4 = 270\ (a'')$
		R(B−Br) = 2.056	$\nu_5 = 304\ (a'),\ \nu_6 = 419\ (a')$
		∠(ClBBr) = 109.47	$\nu_7 = 641\ (a''),\ \nu_8 = 719\ (a')$
		∠(FBBr) = 109.47	$\nu_9 = 1066\ (a')$
$BCl_2Br_2^-$, C_{2v}	5.632	R(B−Cl) = 1.848	$\nu_1 = 137\ (a_1),\ \nu_2 = 156\ (a_2)$
		R(B−Br) = 2.043	$\nu_3 = 211\ (b_2),\ \nu_4 = 221\ (a_1)$
		∠(ClBBr) = 109.47	$\nu_5 = 241\ (b_1),\ \nu_6 = 351\ (a_1),\ \nu_7 = 629\ (b_2),\ \nu_8 = 696\ (a_1),\ \nu_9 = 748\ (b_1)$
$BFBr_3^-$, C_{3v}	5.483	R(B−Br) = 2.049	$\nu_1 = 132\ (e),\ \nu_2 = 192\ (a_1)$
		R(B−F) = 1.373	$\nu_3 = 272\ (e),\ \nu_4 = 363\ (a_1)$
		∠(FBBr) = 109.47	$\nu_5 = 642\ (e),\ \nu_6 = 1070\ (a_1)$
$BClBr_3^-$, C_{3v}	5.575	R(B−Cl) = 1.843	$\nu_1 = 126\ (e),\ \nu_2 = 192\ (a_1)$
		R(B−Br) = 2.037	$\nu_3 = 198\ (e),\ \nu_4 = 305\ (a_1)$
		∠(ClBBr) = 109.47	$\nu_5 = 630\ (e),\ \nu_6 = 728\ (a_1)$
BBr_4^-, T_d	5.625	R(B−Br) = 2.032	$\nu_1 = 112\ (e),\ \nu_2 = 168\ (f_2)$
		∠(BrBBr) = 109.47	$\nu_3 = 247\ (a_1),\ \nu_4 = 631\ (f_2)$

[a] Bond lengths (R) in Ångstroms, valence angles (∠) in degrees, vertical electron detachment energies in electronvolts.

$BF_2Cl_2^-$, $AlF_2Br_2^-$, $AlCl_2Br_2^-$, and $AlF_2Cl_2^-$), and C_s ($BFClBr_2^-$, $BFCl_2Br^-$, BF_2ClBr^-, $AlFClBr_2^-$, $AlFCl_2Br^-$, and AlF_2ClBr^-) symmetry. This finding is consistent with the earlier calculations performed by others for AlF_4^- and BF_4^-, in which T_d-symmetry geometries were found.[19] In addition, we checked that lower symmetry structures are not geometrically stable (e.g., we confirmed that the planar AlF_4^- and BF_4^- do not correspond to the minimum energy structures and the deformation along their imaginary modes lead to tetrahedral T_d species).

The B−F and Al−F bond lengths for the optimized anions are within the 1.373−1.415 Å and 1.701−1.716 Å ranges, respectively, and we found the largest B−F and Al−F separations for BF_4^- and AlF_4^- species (see Tables 1 and 2). On the other hand, the shortest B−F and Al−F bond lengths were observed for the anions containing three Br atoms and only one F atom ($BFBr_3^-$ and $AlFBr_3^-$). Data collected in Table 1 demonstrate that the B−X distance decreases when the X atom in BX_4^- is replaced with the less electronegative one, whereas the reverse situation is observed when the replacing atom is more electronegative than X. This effect is obviously also connected with the higher ionic character of the bonds (the higher the ionicity, the longer the bond length). To illustrate, the shortening of the B−F bond length by ca. 0.012−0.017 Å accompanies the substitution of the fluorine atom with chlorine and bromine. Similarly, the ca. 0.005−0.017 Å elongation of the B−Br distance is observed when the bromine atom in BBr_4^-

Table 2. The MP2 Geometrical Parameters, Corresponding Harmonic Vibrational Frequencies, and the OVGF/6-311+G(3df) VDEs for the AlX_4^- (X = F, Cl, Br) Anions Studied in This Work[a]

species and symmetry point group	VDE^{OVGF} 6−311+G(3df)	geometry	frequencies [cm^{-1}]
AlF_4^-, T_d	9.789	R(Al−F) = 1.716 ∠(FAlF) = 109.47	$\nu_1 = 193\ (e)$, $\nu_2 = 301\ (f_2)$ $\nu_3 = 605\ (a_1)$, $\nu_4 = 780\ (f_2)$
AlF_3Cl^-, C_{3v}	7.245	R(Al−F) = 1.711 R(Al−Cl) = 2.165 ∠(FAlCl) = 109.47	$\nu_1 = 165(e)$, $\nu_2 = 267\ (e)$ $\nu_3 = 271\ (a_1)$, $\nu_4 = 462\ (a_1)$ $\nu_5 = 673\ (a_1)$, $\nu_6 = 789\ (e)$
$AlF_2Cl_2^-$, C_{2v}	6.990	R(Al−F) = 1.707 R(Al−Cl) = 2.158 ∠(FAlCl) = 109.47	$\nu_1 = 137\ (a_1)$, $\nu_2 = 153\ (a_2)$ $\nu_3 = 218\ (b_2)$, $\nu_4 = 246\ (b_1)$ $\nu_5 = 250\ (a_1)$, $\nu_6 = 420\ (a_1)$, $\nu_7 = 518\ (b_1)$, $\nu_8 = 725\ (a_1)$, $\nu_9 = 798\ (b_2)$
$AlFCl_3^-$, C_{3v}	6.934	R(Al−F) = 1.704 R(Al−Cl) = 2.153 ∠(FAlCl) = 109.47	$\nu_1 = 127\ (e)$, $\nu_2 = 190\ (a_1)$ $\nu_3 = 220\ (e)$, $\nu_4 = 384\ (a_1)$ $\nu_5 = 518\ (e)$, $\nu_6 = 768\ (a_1)$
AlF_3Br^-, C_{3v}	6.519	R(Al−F) = 1.709 R(Al−Br) = 2.344 ∠(FAlBr) = 109.47	$\nu_1 = 149\ (e)$, $\nu_2 = 221\ (a_1)$ $\nu_3 = 261\ (e)$, $\nu_4 = 397\ (a_1)$ $\nu_5 = 666\ (a_1)$, $\nu_6 = 794\ (e)$
$AlCl_4^-$, T_d	7.016	R(Al−Cl) = 2.149 ∠(ClAlCl) = 109.47	$\nu_1 = 115\ (e)$, $\nu_2 = 180\ (f_2)$ $\nu_3 = 355\ (a_1)$, $\nu_4 = 519\ (f_2)$
AlF_2ClBr^-, C_s	6.475	R(Al−F) = 1.706 R(Al−Cl) = 2.156 R(Al−Br) = 2.336 ∠(FAlCl) = 109.47 ∠(FAlBr) = 109.47	$\nu_1 = 118\ (a')$, $\nu_2 = 143\ (a'')$ $\nu_3 = 206\ (a')$, $\nu_4 = 208\ (a')$ $\nu_5 = 244\ (a')$, $\nu_6 = 366\ (a')$ $\nu_7 = 490\ (a')$, $\nu_8 = 723\ (a')$ $\nu_9 = 801\ (a'')$
$AlFCl_2Br^-$, C_s	6.494	R(Al−F) = 1.703 R(Al−Cl) = 2.151 R(Al−Br) = 2.332 ∠(ClAlBr) = 109.47 ∠(FAlBr) = 109.47	$\nu_1 = 110\ (a'')$, $\nu_2 = 117\ (a')$ $\nu_3 = 174\ (a')$, $\nu_4 = 192\ (a')$ $\nu_5 = 214\ (a'')$, $\nu_6 = 334\ (a')$ $\nu_7 = 471\ (a')$, $\nu_8 = 520\ (a'')$ $\nu_9 = 769\ (a')$
$AlCl_3Br^-$, C_{3v}	6.545	R(Al−Cl) = 2.147 R(Al−Br) = 2.329 ∠(ClAlBr) = 109.47	$\nu_1 = 103\ (e)$, $\nu_2 = 155\ (a_1)$ $\nu_3 = 168\ (e)$, $\nu_4 = 310\ (a_1)$ $\nu_5 = 457\ (a_1)$, $\nu_6 = 522\ (e)$
$AlF_2Br_2^-$, C_{2v}	6.286	R(Al−F) = 1.704 R(Al−Br) = 2.334 ∠(FAlBr) = 109.47	$\nu_1 = 95\ (a_1)$, $\nu_2 = 136\ (a_2)$ $\nu_3 = 190\ (b_1)$, $\nu_4 = 202\ (b_2)$ $\nu_5 = 212\ (a_1)$, $\nu_6 = 337\ (a_1)$, $\nu_7 = 429\ (b_2)$, $\nu_8 = 721\ (a_1)$, $\nu_9 = 804\ (b_1)$
$AlFClBr_2^-$, C_s	6.329	R(Al−F) = 1.702 R(Al−Cl) = 2.148 R(Al−Br) = 2.329 ∠(ClAlBr) = 109.47 ∠(FAlBr) = 109.47	$\nu_1 = 91\ (a')$, $\nu_2 = 108\ (a'')$ $\nu_3 = 156\ (a')$, $\nu_4 = 182\ (a'')$ $\nu_5 = 195\ (a')$, $\nu_6 = 302\ (a')$ $\nu_7 = 424\ (a'')$, $\nu_8 = 501\ (a')$ $\nu_9 = 769\ (a')$
$AlCl_2Br_2^-$, C_{2v}	6.375	R(Al−Cl) = 2.146 R(Al−Br) = 2.326 ∠(ClAlBr) = 109.47	$\nu_1 = 86\ (a_1)$, $\nu_2 = 95\ (a_2)$ $\nu_3 = 144\ (b_2)$, $\nu_4 = 148\ (a_1)$ $\nu_5 = 152\ (b_1)$, $\nu_6 = 277\ (a_1)$, $\nu_7 = 419\ (b_2)$, $\nu_8 = 485\ (a_1)$, $\nu_9 = 523\ (b_1)$
$AlFBr_3^-$, C_{3v}	6.258	R(Al−Br) = 2.327 R(Al−F) = 1.701 ∠(FAlBr) = 109.47	$\nu_1 = 86\ (e)$, $\nu_2 = 134\ (a_1)$ $\nu_3 = 178\ (e)$, $\nu_4 = 269\ (a_1)$ $\nu_5 = 423\ (e)$, $\nu_6 = 771\ (a_1)$
$AlClBr_3^-$, C_{3v}	6.313	R(Al−Cl) = 2.144 R(Al−Br) = 2.324 ∠(ClAlBr) = 109.47	$\nu_1 = 79\ (e)$, $\nu_2 = 130\ (a_1)$ $\nu_3 = 133\ (e)$, $\nu_4 = 246\ (a_1)$ $\nu_5 = 420\ (e)$, $\nu_6 = 507\ (a_1)$
$AlBr_4^-$, T_d	6.346	R(Al−Br) = 2.322 ∠(BrAlBr) = 109.47	$\nu_1 = 71\ (e)$, $\nu_2 = 115\ (f_2)$ $\nu_3 = 214\ (a_1)$, $\nu_4 = 420\ (f_2)$

[a] Bond lengths (R) in Ångstroms, valence angles (∠) in degrees, vertical electron detachment energies in electronvolts.

is replaced with a chlorine or fluorine atom (see Table 1). As far as the superhalogen anions containing Al are concerned, the subsequent substitution of F atoms with Cl atoms in AlF_4^- leads to a shortening of the Al−F bond by 0.005−0.012 Å, while an elongation of the Al−Br bond length in $AlBr_4^-$ (by 0.002−0.022 Å) is observed when the bromine atoms are replaced with fluorine and/or chlorine atoms (see Table 2).

Since the experimental data for the mixed (i.e., containing various superhalogen ligands) anions are not available, we compare our B−F distance for BF_4^- to the experimental B−F bond length (1.3785−1.391 Å) obtained by Haiges et al.[29] and our Al−F distance for AlF_4^- to the experimental bond length (1.69 Å) reported by Blander et al.[30] The differences between the bond lengths calculated by us and the experimental values are 0.0365−0.024 and 0.026 Å for M−F distances in BF_4^- and AlF_4^-, respectively, and similar discrepancies were also observed in ref 19 (where the CCSD(T) and MBPT(4) methods were employed for optimizing the geometry). As far as the B−Cl and Al−Cl bond lengths (for BCl_4^- and $AlCl_4^-$, respectively) are concerned, we also observe good agreement between the experimental values and the distances calculated by us. The experimental B−Cl bond length for BCl_4^- was found to be 1.84 Å,[31] while our estimate of this distance is 1.86 Å (see Table 1). Similarly, we compare our 2.149 Å Al−Cl separation in $AlCl_4^-$ (see Table 2) to the 2.11−2.16 Å experimental bond length described in ref 29. According to this comparison, we conclude that one should expect similar discrepancies between the experimental bond lengths (when they become available) for the "mixed" BX_4^- and AlX_4^- anions (where X = F, Cl, Br) and our values collected in Tables 1 and 2.

Even though the reported geometry differences seem relatively small, it should be noted that they could play an important role in superhalogen species because the halogen−central atom distance significantly influences the vertical electron detachment energy of such anions, as was previously concluded by Gutsev and Boldyrev.[4]

The calculated harmonic vibrational frequencies for all 30 anions are collected in Tables 1 and 2 without scaling. Again, because of the lack of the experimental data for the "mixed" systems, we compare our results only for four basic species, that is, BF_4^-, BCl_4^-, AlF_4^-, and $AlCl_4^-$. As we noted, the frequencies obtained at the MP2 level are in a relatively good agreement with those measured by Christe et al.[32] (for BF_4^-) and Gilbert et al.[33] (for AlF_4^-). In particular, for BF_4^-, our MP2-calculated frequencies are always shifted down (by 1−31 cm^{-1}) with respect to the experimental ones, with the smallest difference for the most stiff f_2 modes and the largest discrepancy for the fully symmetric a_1 modes. A similar situation is observed in the AlF_4^- case, where almost all values are shifted down by 17−20 cm^{-1} with respect to the experimental findings. Only the stiffest f_2 modes (triply degenerate ν_4, see Table 2) are shifted up by 20 cm^{-1} compared to the experimentally measured vibrations.[33] As far as the vibrational frequencies for BCl_4^- and $AlCl_4^-$ are concerned, our results are usually shifted up compared to the experimental values. For BCl_4^-, the differences between our frequencies (collected in Table 1) and the measured values (taken from ref 34) are in the 7−41 cm^{-1} range, with the smallest difference for the softest degenerate *e*-symmetry modes and the largest discrepancy for the stiffest f_2 modes. Even small differences (in the 2−21 cm^{-1} range) are observed for the vibrational modes calculated for $AlCl_4^-$. Namely, compared to the experimental results described in ref 35, the largest discrepancy between our frequencies and those measured by Rytter and Øye is 21 cm^{-1} for the stiffest f_2 modes (triply degenerate ν_4, see Table 2), while the smallest difference (2 cm^{-1}) is observed for the softer f_2 vibrations (ν_2 in Table 2). These findings make us believe that also other vibrational frequencies for the yet experimentally unknown "mixed" superhalogen anions that we report in this contribution should be in good agreement with the real ones. Our hope is that experimental chemists will find these data useful while synthesizing BX_4^- and AlX_4^- species in the near future and in determining their IR spectra.

Table 3. The VDEs (in eV) of all Superhalogen Anions Studied in This Work Calculated at the MP2 and OVGF Levels with the 6-311+G(3df) Basis Sets

species	VDE^{MP2}	VDE^{OVGF}	species	VDE^{MP2}	VDE^{OVGF}
BF_4^-	8.006	8.975	AlF_4^-	8.716	9.789
BF_3Cl^-	6.391	6.428	AlF_3Cl^-	7.168	7.245
$BF_2Cl_2^-$	6.037	6.089	$AlF_2Cl_2^-$	6.909	6.990
$BFCl_3^-$	5.940	6.076	$AlFCl_3^-$	6.795	6.934
BF_3Br^-	5.684	5.729	AlF_3Br^-	6.439	6.519
BCl_4^-	6.025	6.218	$AlCl_4^-$	6.837	7.016
BF_2ClBr^-	5.713	5.653	AlF_2ClBr^-	6.459	6.475
$BFCl_2Br^-$	5.794	5.712	$AlFCl_2Br^-$	6.494	6.494
BCl_3Br^-	5.906	5.827	$AlCl_3Br^-$	6.537	6.545
$BF_2Br_2^-$	5.423	5.456	$AlF_2Br_2^-$	6.228	6.286
$BFClBr_2^-$	5.517	5.545	$AlFClBr_2^-$	6.275	6.329
$BCl_2Br_2^-$	5.590	5.632	$AlCl_2Br_2^-$	6.312	6.375
$BFBr_3^-$	5.400	5.483	$AlFBr_3^-$	6.171	6.258
$BClBr_3^-$	5.467	5.575	$AlClBr_3^-$	6.207	6.313
BBr_4^-	5.506	5.625	$AlBr_4^-$	6.235	6.346

3.2. Vertical Electron Detachment Energies. The vertical electron detachment energies of MX_4^- (M = B, Al; X = F, Cl, Br) anions calculated at the OVGF/6-311+G(3df) level (VDE^{OVGF}) are collected in Tables 1 and 2, while those obtained at the MP2 level with the 6-311+G(3df) basis sets (VDE^{MP2}) are shown in Table 3 for comparison. On the basis of our and others' experience,[13] we consider the VDEs calculated at the OVGF level with the 6-311+G(3df) basis sets as the most reliable results, and we limit our discussion to these values. The only issue we want to raise considering this comparison is the observation that the VDEs are usually underestimated at the MP2 level of theory (with respect to the OVGF values). In the few cases for which VDE^{OVGF} < VDE^{MP2}, the differences between these values are smaller than 0.1 eV, which covers approximately less than 2% of the VDE. Therefore, one may neglect and assume that, for these species, that is, superhalogen anions having B or Al as the central atoms, the MP2 estimates of the VDE are not larger than the preferred vertical electron detachment energies (approximated here by the VDE^{OVGF}). In most cases, the differences between VDE^{OVGF} and VDE^{MP2} are within the 0.01−0.19 eV range, see Table 3. However, for two species, namely, BF_4^- and AlF_4^-, these discrepancies are much larger and approach 1 eV. Analogous behavior was also observed in the symmetrical (i.e., not "mixed") superhalogens containing other central atoms, such as Be, Mg, and Ca, and F ligands.[13,14] Therefore, we conclude that the MP2 method allows for an easy and fast estimate of the electronic stability of a superhalogen anion when neither experimental nor theoretical results are available. One should keep in mind, however, that such MP2 results will likely be underestimated, especially when the MF_{k+1}^- anions are studied (where *k* stands for the maximum formal valence of the central atom M).

Now, we move on to the discussion of the vertical electron detachment energies obtained at the OVGF/6-311+G(3df) level for 30 BX_4^- and AlX_4^- anions studied in this contribution. First, we want to stress that all of the calculated VDEs greatly exceed the electron affinity of the chlorine atom (3.62 eV), and thus the studied BX_4^- and AlX_4^- species should be classified as the superhalogen anions. The largest VDE among systems considered was found for AlF_4^- (9.789

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eV) and for BF_4^- (8.975 eV). The vertical electron detachment energies of the remaining anions are always larger than 5.4 eV (see Tables 1 and 2), which suggests that all of these species can potentially act as strong electron acceptors.

In the BF_4^-−BCl_4^-−BBr_4^- series, the VDE decreases from 8.975 to 5.625 eV, which is consistent with our earlier conclusion on the dependence of the electronic stability of superhalogen anions on the ligands of which those anions consist.[13] This significant decrease of the VDE value caused by replacing four F ligands with either four Cl or four Br atoms shows that the larger the ligand is, the smaller the vertical electron detachment energy of the resulting superhalogen anion is. A similar tendency can be observed in the AlF_4^-−$AlCl_4^-$−$AlBr_4^-$ series, in which the VDE also decreases (from 9.789 to 6.346 eV) with an increase of the atomic number of the halogen atoms used as ligands.

The analysis of the results calculated for BF_4^-, BF_3Cl^-, and BF_3Br^- indicates that replacing the fluorine atom in BF_4^- with Cl or Br also leads to a lower VDE (by 2.547 and 3.246 eV, respectively), which is again accompanied by a shortening of the B−F bond (see Table 1). We observe the same situation for AlF_4^-, in which one F atom is replaced with Cl or Br, leading to AlF_3Cl^- or AlF_3Br^-, respectively. Specifically, the VDE of AlF_4^- (9.789 eV, see Table 2) decreases by 2.544 eV when one fluorine atom is replaced with chlorine and by 3.270 eV when the fluorine atom is replaced with bromine. This is also accompanied by a shortening of the Al−F bond (see Table 2). The shortening of the B−F and Al−F bond lengths observed when the fluorine atoms in BF_4^- or AlF_4^- are being subsequently substituted with chlorine or bromine causes additional destabilizing effects due to the more limited excess electron delocalization in the negatively charged species. This observation may suggest that replacing only one small ligand in the superhalogen system with the larger atom is highly unfavorable because it leads unexpectedly to a significantly lower VDE, as was also found in ref 15.

In order to support our discussion, we present the three-dimensional pictures of the HOMO for representative anions (see Figures 1 and 2). As can be seen for three "symmetrical" (T_d), "nonmixed" anions (i.e., the anions built of the same four ligands: BF_4^-, BCl_4^-, BBr_4^-, AlF_4^-, BCl_4^-, and $AlBr_4^-$), the corresponding highest occupied molecular orbitals (HOMOs) are composed purely of ligands' atomic orbitals (AOs), see Figure 1. As a consequence, these HOMOs display a nonbonding ligand−central atom character, as predicted earlier by Boldyrev and Gutsev[4] and confirmed by others. In contrast, for the "mixed" anions, the HOMO is composed not only of ligands' AOs but also of B or Al AOs (see Figure 2, where small lobes on the central Al atom are shown in the case of AlF_3Br^-). Therefore, each of the HOMOs for the "mixed" systems exhibits both a bonding character between the central atom and the smaller (more electronegative) ligand and an antibonding interaction between the central atom and the larger (less electronegative) ligand. This observation is consistent with the changes in the bond lengths that could be derived from Tables 1 and 2 and were discussed in the preceding paragraphs and section 3.1. For example, the B−Cl distance in $BClBr_3^-$ is shorter than the corresponding boron−chlorine bond length in BCl_4^-, while the B−Br bond length in BCl_3Br^- is longer than those in BBr_4^- (see Table 1). The same tendency can be observed for the Al−Cl bond length (see Table 2) when one or more chlorine atoms in $AlCl_4^-$ are subsequently replaced with bromine atoms (which leads to $AlCl_3Br^-$, $AlCl_2Br_2^-$, etc.).

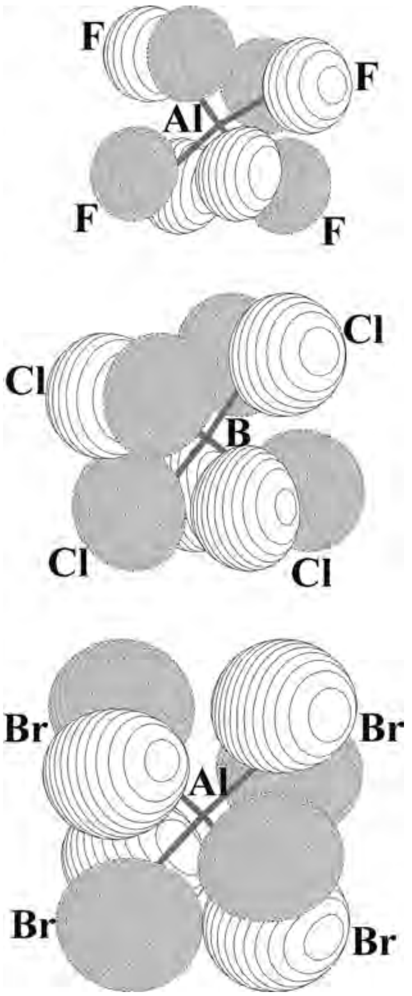

Figure 1. The highest occupied molecular orbitals of the representative T_d-symmetry anions: AlF_4^-, BCl_4^-, and $AlBr_4^-$.

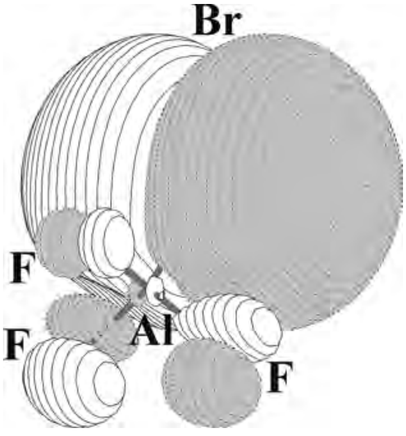

Figure 2. The highest occupied molecular orbital of the representative "mixed" AlF_3Br^- anion where the contribution from the Al's AOs can be seen.

On the basis of our results gathered in Tables 1 and 2 and depicted in Figures 1 and 2, we conclude that replacing only one halogen ligand with a less electronegative atom causes a surprisingly rapid decrease of the VDE of the corresponding superhalogen anion, which can be explained by the change of the HOMO nature in the resulting system. Namely, the original nonbonding HOMO in a T_d-symmetry species, such as BF_4^- or $AlCl_4^-$, changes to a mixed bonding/antibonding character when one of the ligands is replaced with a different halogen atom. This change in the HOMO nature is naturally accompanied by a shortening of the bond length connecting the central atom and the smaller ligand and by an elongation of the distance between the less negative ligand and the central atom (with respect to those in BF_4^-, BCl_4^-, BBr_4^-, AlF_4^-, $AlCl_4^-$ and $AlBr_4^-$ species). These conclusions are in agreement with our previous findings formulated recently for the NaX_2^- superhalogen anions (where X = F, Cl, Br).[15] Therefore, we point out that the simple rule formulated in the past and stating that the smaller the ligands are, the larger the electronic stability of the resulting superhalogen anions is seems oversimplified and should be reformulated. Indeed, having fluorine atoms as ligands in the superhalogen systems leads to significantly larger VDEs but with the reservation that one should use the same halogen atoms, which allows for a higher symmetry of the system and preserves the desirable nonbonding nature of its HOMO.

4. Summary

The vertical electron detachment energies of 30 superhalogen anions BX_4^- and AlX_4^- (X = F, Cl, Br) were calculated at the OVGF/6-311+G(3df) level. All of the negatively charged species studied in this work were derived from their neutral parent radicals and have proven to exhibit a "superhalogen" nature, which means that their electron binding energies were found to significantly exceed the electron affinity of the chlorine atom (3.62 eV). It was concluded that the OVGF/6-311+G(3df) treatment produces reliable estimates of the previously studied superhalogen anions, and the following vertical detachment energies of 30 MX_4^- (M = B, Al; X = F, Cl, Br) species considered in this work are given in Table 3. In this contribution, we also confirmed that the desirable nonbonding nature of the HOMO in superhalogen anions is broken when different halogen atoms are used as ligands. In such mixed systems, the HOMO is no longer nonbonding but exhibits both bonding and antibonding character (with respect to the central atom and various ligands), and these effects are accompanied by bond lengths changes. The changes in the HOMO nature triggered by the introduction of various halogen ligands into the superhalogens reduce the vertical electron detachment energies of the resulting anions.

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