A theoretical study of boron tetrahalides: Structures and electron affinities

Daniel J. Goebbert *

Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, AL 35487, United States

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ABSTRACT

A series of superhalogens, the boron tetrahalides, $BF_nCl_m^-$, $n + m = 4$, were studied at the B3LYP/aug-cc-pVTZ level of theory. Their adiabatic detachment energies, vertical detachment energies and geometries were the focus of this study. All molecules have large adiabatic detachment energies of 6.83, 4.97, 5.07, 5.23 and 5.27 eV for $n = 4$–0 respectively. The neutral molecules have two low energy isomers, with the exception of BF_3Cl, that have very different geometries. These isomers are classified as non-covalent complexes with a halogen atom solvated by a boron trihalide, or a covalent structure with shorter B–F and B–Cl bonds. The covalent structure has not been reported in earlier studies. Our study indicates that all neutrals are weakly bound with low barriers for isomerization. All neutral covalent structures appear to be metastable with respect to isomerization and/or dissociation.

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1. Introduction

Molecules with adiabatic detachment energies (ADEs) greater than that of atomic fluorine or chlorine (ADE = 3.401 and 3.614 eV respectively) [1,2] are an important group of chemical species classified as superhalogens. These molecules are extreme oxidizers [3,4] and have found use in the synthesis of unusual molecules, including Nobel gas compounds [5]. Superhalogens are classified by relative strength, requiring accurate adiabatic detachment energies (also commonly referred to as electron affinities). Of the numerous experimental techniques for measuring ADEs, gas phase photoelectron spectroscopy usually provides ADEs with unparalleled accuracy [6–9]. Successful photoelectron spectroscopy of superhalogens requires high intensity and high energy photons. Because of their large electron affinities, the photon energy needed for electron detachment of superhalogens is often beyond the range of most commercial laser systems [10,11]. Therefore, it is critical to obtain accurate predictions of their electron affinities.

One class of superhalogen anions that has been generated in the gas-phase are boron tetrahalide anions, such as BF_4^-, BF_3Cl^- and BCl_4^- [12–20]. The dissociation energies of some of these anions have been experimentally measured [14,20], although experimental electron binding energies remain unmeasured. There have been a few theoretical studies of the boron tetrahalides [21–23]. Gutsev et al. studied BF_4/BF_4^- at the MBPT(4) and CCSD(T) levels of theory [21]. Their calculations predicted a non-covalent structure for BF_4, which has one long B–F bond and three short, nearly planar B–F bonds essen-

tially forming a BF_3 molecule. The anion BF_4^- was calculated to be tetrahedral with bond lengths of 1.410 Å. The non-covalent structure of BF_4 was calculated to have an adiabatic detachment energy of 6.75 eV, significantly larger than what might be expected for a solvated fluorine atom. More recently, Anusiewicz and coworkers carried out a study of BX_4^- superhalogen anions at the OVGF/6-311+G(3df) level of theory [23]. However, this study yielded vertical detachment energies (VDEs), not adiabatic detachment energies. The vertical detachment energy for BF_4^- was calculated to be 8.975 eV, much larger than the reported ADE of 6.75 eV.

Previous theoretical studies on BF_4 are similar to another early paper on neutral donor–acceptor complexes of BH_3 or BF_3 with CO and NH_3. This study investigated these non-covalent complexes at the MP2/6-31+G** level of theory [24]. All complexes were characterized by long B–C or B–N bonds from the lone pairs of CO or NH_3, with longer bond lengths for BF_3 complexes compared to the same BH_3 complexes. The longer bonds of BF_3 complexes are due to π donation from the fluorine atom lone pairs into the empty boron p_z orbital. The π electron donation increases the relative energy of the LUMO in BF_3 relative to the HOMO of CO or NH_3.

It is instructive to analyze the $BF_3 + F$ interaction for BF_4 formation. Although a universal scale for Lewis acidity does not exist, the acidity of BF_3 is usually considered to be lower than other prototypical Lewis acids such as BH_3. The decreased acidity is often attributed to π electron donation from F atom lone pairs by invoking resonance structures with a negatively charged B atom and positively charged F atom [22]. Formation of BF_4 requires electron donation from F· into the empty boron p_z orbital of BF_3. This could be either a lone pair, or single electron interaction. This suggests the possibility of at least two different bonding interactions, consequently at least two different BF_4 isomers. In contrast to

* Tel.: +1 205 348 2206; fax: +1 205 348 9104.
  E-mail address: djgoebbert@bama.ua.edu

the neutral, only lone pair electron donation is possible in the formation of BF_4^- from BF_3 and F^-, or other boron tetrahalides.

In this paper we report a theoretical study of the boron tetrahalide series BF_nCl_m, $n + m = 4$. Our results will be compared to available data from earlier theoretical studies. The goal of our study was to calculate electron affinities and trends, and also to obtain equilibrium geometries of both the anion and neutral molecules. While we might expect BF_4 to have a large ADE, it is difficult to predict the effect of Cl substitution. The large electron affinity and polarizability of Cl atoms compared to F atoms help stabilize negative charges, and these properties should play an integral role in ADE trends as a function of Cl substitution. We might expect that sequential Cl substitution will be reflected in increases ADEs (i.e. $BF_3Cl < BF_2Cl_2 < BFCl_3 < BCl_4$). However, in the previous study of boron halide VDEs at the OVGF level of theory the trend was: $BFCl_3 < BF_2Cl_2 < BCl_4 < BF_3Cl$ [23]. In that study, the energies do not account for geometry relaxation between the most stable anion and neutral geometries. Therefore, a major factor in elucidating the expected trend in ADEs is the difference in equilibrium geometry between anion and neutral. This distinction between VDE and ADE is crucial for properly classifying relative superhalogen strengths and for designing experiments that confirm theoretical predictions.

2. Computational details

All calculations were carried out using the Gaussian 03 [25] software using density functional theory with the B3LYP [26–28] functional. The B3LYP functional usually gives reliable electron affinities, sufficient for comparison to experimental data. The 6-31+G(d) [29–33], and aug-cc-pVTZ [34,35] basis sets were used, but we refer almost exclusively to the aug-cc-pVTZ results except where noted. Optimized geometries were calculating using SCF convergence criteria of $10^{-8}E_h$ on a grid of 75 radial shells and 302 angular points per shell per atom and the convergence criteria were set to 10^{-5} rms for the force constants and 4×10^{-4} for the rms atomic displacements. Vibrational frequencies were calculated within the harmonic approximation to evaluate if the minima were stationary points defined as having zero imaginary frequencies. Vertical detachment energies were calculated from the energy difference between the anion and neutral with a fixed geometry using the anion equilibrium structure. Adiabatic detachment energies were calculated from the energy difference between anion and neutral at their respective equilibrium geometries. Vertical attachment energies, VAEs, were calculated from the energy difference between the anion and neutral with a fixed geometry using the equilibrium structure of the neutral molecule. All energies are reported as absolute electronic energy differences and energy differences including zero-point corrections. The adiabatic detachment energy and vertical attachment energies are properties of the neutral boron tetrahalides, while vertical detachment energy is a property of the anion.

In order to aid our interpretation of some results we carried out relaxed potential energy surface scans for the neutral molecules at the B3LYP/6-31+G(d) level of theory. These calculations scanned the energy over a range of fixed B–F or B–Cl bond distances, while allowing all other geometry parameters to optimize. The smaller basis set makes these calculations rather crude but survey studies showed that larger basis sets given nearly identical results, sufficient for semi-quantitative comparison.

3. Results and discussion

The optimized geometries of the boron halide anions, $BF_nCl_m^-$ at the B3LYP/aug-cc-pVTZ level of theory are shown in Fig. 1. A sum-
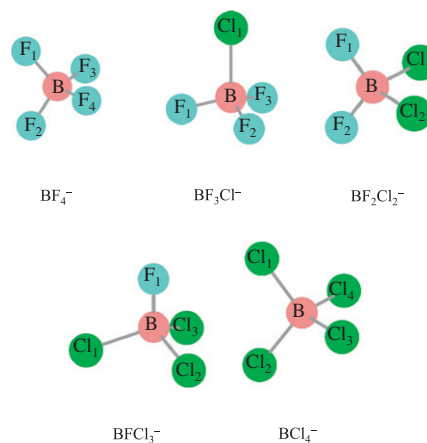

Fig. 1. The optimized structures for BF_4^-, BF_3Cl^-, $BF_2Cl_2^-$, $BFCl_3^-$ and BCl_4^- at the B3LYP/aug-cc-pVTZ level of theory are shown. The atom labels are used for defining the geometry parameters listed in Table 1. All anions are covalent with high symmetry.

mary of the critical geometry parameters, point group and vibrational energies for each ion is listed in Table 1, while the vertical detachment energies are listed in Table 2. All anions have global minima with highly symmetric structures. There is a decrease in both B–F and B–Cl bond lengths with increasing Cl substitution. For most anions, the bond angles are nearly tetrahedral, the largest deviation is for BF_3Cl^-, which has an F–B–F bond angle of 111.43°.

The optimized geometries for the neutral boron tetrahalides, BF_nCl_m at the B3LYP/aug-cc-pVTZ level of theory are shown in Fig. 2. A summary of critical geometry parameters, vibrational energies are listed in Table 3, while ADE and VAE values are listed in Table 2. As expected, the ADE values are bracketed by the VDEs on the high end and VAEs on the low end. The effect of zero-point corrections on the VDE, ADE and VAE are generally minimal. We located two different minimum energy structures for BF_4, BF_2Cl_2, $BFCl_3$ and BCl_4. These structures are classified as non-covalent (isomer type I) or covalent (isomer type II). The lone exception is BF_3Cl which did not converge to the isomer II geometry. The labels I or II are not used to specify the global minimum, but merely as a label for identifying the geometry. All isomer I molecules essentially

Table 1
Optimized anion geometries, vibrational frequencies and vertical detachment energies calculated at the B3LYP/aug-cc-pVTZ level of theory.

Species and symmetry point group	Geometry[a]	Frequencies (cm^{-1})
BF_4^-, T_d	R(F$_1$–B) = 1.412 ∠(F$_1$BF$_2$) = 109.47	340 (e), 508 (t$_2$), 751 (a$_1$), 1050 (t$_2$)
BF_3Cl^-, C_{3v}	R(F$_1$–B) = 1.387 R(Cl$_1$–B) = 1.981 ∠(F$_1$BF$_2$) = 111.43 ∠(F$_1$BCl$_1$) = 107.43	264 (e), 328 (a$_1$), 461 (e), 628 (a$_1$), 841 (a$_1$), 1118 (e)
$BF_2Cl_2^-$, C_{2v}	R(F$_1$–B) = 1.375 R(Cl$_1$–B) = 1.927 ∠(F$_1$BF$_2$) = 112.30 ∠(F$_1$BCl$_1$) = 108.95 ∠(Cl$_1$BCl$_2$) = 108.67	201 (a$_1$), 253 (a$_2$), 339 (b$_1$), 353 (b$_2$), 360 (a$_1$), 556 (a$_1$), 643 (b$_1$), 976 (a$_1$), 1143 (b$_2$)
$BFCl_3^-$, C_{3v}	R(F$_1$–B) = 1.368 R(Cl$_1$–B) = 1.900 ∠(F$_1$BCl$_1$) = 109.75 ∠(Cl$_1$BCl$_2$) = 109.20	194 (e), 282 (a$_1$), 328 (e), 445 (a$_1$), 646 (e), 1080 (a$_1$)
BCl_4^-, T_d	R(Cl$_1$–B) = 1.879 ∠(Cl$_1$BCl$_2$) = 109.47	178 (e), 264 (t$_2$), 391 (a$_1$), 652 (t$_2$)

[a] Bond lengths reported in Å and angles in degrees.