



## Classroom Article

Formation of argon–boron bonds in the reactions of  $\text{BF}_n^{+/2+}$  cations with neutral argon

Lauren Levee<sup>a</sup>, Catherine Calogero<sup>a</sup>, Edward Barbieri<sup>a</sup>, Steven Byrne<sup>a</sup>, Courtney Donahue<sup>a</sup>, Michael Eisenberg<sup>b</sup>, Sean Hattenbach<sup>a</sup>, Julie Le<sup>a</sup>, Joseph F. Capitani<sup>a</sup>, Jana Roithová<sup>c</sup>, Detlef Schröder<sup>d,\*</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, Manhattan College, Riverdale, NY 10471, USA

<sup>b</sup> Department of Chemical Engineering, Manhattan College, Riverdale, NY, 10471, USA

<sup>c</sup> Department of Organic Chemistry, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic

<sup>d</sup> Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo náměstí 2, 16610 Prague 6, Czech Republic

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## ABSTRACT

Experimental data on the reactions of argon with  $\text{BF}_n^+$  monocations ( $n=0-3$ ) and  $\text{BF}_n^{2+}$  dications ( $n=1, 2$ ) and dications reveal the formation of the new argon species  $\text{ArBF}_2^+$  and  $\text{ArBF}_2^{2+}$ . Theoretical calculations on the stability of these ions using density functional theory confirm the formation of the rare-gas compounds, but their formation is only exothermic for the reaction  $\text{Ar} + \text{BF}_2^{2+} \rightarrow \text{ArBF}_2^{2+} + \text{F}$ . According to theory, the corresponding neon compounds all involve endothermic pathways and could hence only be formed via involvement of excited states.

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## 1. Introduction

Recently, we have found that several small gaseous dications can act as sufficiently superelectrophilic reagents [1] to promote the formation of bonds between rare gases and other elements than fluorine, which is the most common bonding partner in rare-gas compounds [2]. For example, by the use of gaseous dications [3,4] the organo-rare-gas compounds  $\text{ArCH}_2^+$  [5],  $\text{ArCF}_2^{2+}$  [6], and  $\text{ArCCH}_2^{2+}$  [7] could have been generated, thereby verifying a prediction made earlier for halocarbenes [8]. Recently, several other hydrocarbon-rare gas adducts have also been generated via ion/molecule reactions of gaseous dications [9–11]. In a deliberate strategy attempting to maximize the yield of rare-gas compounds, the silicon derivatives  $\text{NeSiF}_2^{2+}$  and  $\text{ArSiF}_2^{2+}$  were generated in the reaction of mass-selected  $\text{SiF}_3^{2+}$  with neon and argon, respectively [12,13]. Likewise, gas-phase ion chemistry has recently been successfully applied to generate novel rare-gas species such as  $\text{XeNF}_2^+$  [14] and  $\text{XeGeF}_3^+$  [15]. Accordingly, similar approaches might enable the formation of species having bonds between boron and rare gases [16]; for the related synthesis of  $\text{FXeBF}_2$ , see Refs. [17,18],

and for a theoretical prediction of anionic boron compounds of rare gases, see Refs. [19,20]. In this context we note that the  $\text{ArBF}_2^+$  cation has been observed in the chemical ionization of  $\text{Ar}/\text{BF}_3$  mixtures [21], and that this and the related species  $\text{KrBF}_2^+$  and  $\text{XeBF}_2^+$  as well as the isomeric structures  $\text{FRgBF}^+$  have recently been studied in high-level ab initio calculations parallel to our work [22].

Inspired by results from a teaching course held at the Manhattan College in early 2010, here we report a combined experimental and theoretical study of the reactions of argon with some super-electrophilic  $\text{BF}_n^{+/2+}$  mono- and dications. As documented below, several of the reactions observed in the highly diluted gas phase do indeed lead to the formation of  $\text{Ar}-\text{B}$  bonds and the molecular species reported here may thus inspire research on new rare-gas compounds in condensed media.

## 2. Experimental and theoretical methods

The experiments were performed with a TSQ Classic mass spectrometer [23,24] equipped with an ion source for electron ionization (EI) and an analyzer of QQQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The octopole serving as a collision cell has a separate housing which limits the penetration of gases admitted to the octopole to the vacuum of the manifold. The kinetic energy

\* Corresponding author. Tel.: +420 220 183 117; fax: +420 220 183 583.  
E-mail address: [schroeder@uochb.cas.cz](mailto:schroeder@uochb.cas.cz) (D. Schröder).

of the ions entering the octopole can be varied between 0 and 200 eV, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or collision-induced dissociation (CID) at elevated kinetic energies. The  $\text{BF}_n^{+/2+}$  mono- and dications were generated by EI of  $\text{BF}_3$  gas (Sigma–Aldrich), mass-selected with the first quadrupole (Q1) at a mass resolution fully sufficient to resolve mono- and dications, then reacted with argon admitted to the octopole at a pressure of typically  $3 \times 10^{-4}$  mbar. The bimolecular reactions reported below were recorded at an ion kinetic energy which corresponds to the point of inflection of the curve obtained by retarding-potential analysis. We have shown previously that quasi-thermal reactivity can be monitored under these conditions [25–28]; here, the term quasi-thermal appreciates the fact that the ions' average kinetic energy is indeed close to thermal conditions, while the width of the ions' kinetic energy distribution is not. Note that within the limits of our instrumentation, we could not further cool the cations investigated in this work [4,10]. The mass-selected dications were then reacted with neutral rare gases admitted to the octopole at a typical pressure of  $10^{-4}$  mbar. In some cases, the pressure of the neutral gases was deliberately raised above the single-collision regime [29] in order to investigate consecutive reactions as well as termolecular processes [30]; for a recent detailed study of the dynamics of collisional stabilization, see [31]. Unless otherwise specified, the collision energy was set by changing the offset between the first quadrupole and the octopole, while the offset of Q2 was locked to the sum of the offsets of Q1 and O. The zero-point of the kinetic energy scale as well as the width of the kinetic energy distribution were determined by means of retarding-potential analysis; for the dications reported here, the beam width at half maximum was about  $(5 \pm 1)$  eV in the laboratory frame. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2 operating at unit mass resolution. Typically, about hundred scans were accumulated resulting in an average scan time of 5 min per spectrum.

Due to its corrosive properties, boron trifluoride is harmful for the experimental set-up and significant instabilities of the pressure in the ion source as well as a loss of performance of the filaments in the ion source and in the pressure gauges were observed during the measurements. To keep the damage to the instrumentation at a tolerable level, we hence refrained from extensive kinetic studies of the ion/molecule reactions observed, for which a multipole arrangement anyhow is not ideally suited [30]. Accordingly, we neither convert the relative reactivities found in the experiments into absolute rate constants nor make corrections for the differences in the transmission of the light and heavy product ions to the detector [32,33].

**Note of caution:** While being obvious to chemists routinely working with corrosive gases, we wish to point out an important safety aspect of which mass spectrometrists are not always aware. Thus, prior to any venting or disconnection of a line which contains or has contained a corrosive gas (e.g.,  $\text{BF}_3$ , but the same applies for  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{NO}_x$ , etc.), complete evacuation and subsequent purging of the line is essential. While this operation also helps to avoid unintended contact with the gas, the major purpose is the protection of the gas bottle itself. If this pumping step is omitted, rests of the gases in the line react with the humidity in the laboratory air to yield strong acids as droplets of fluid, which often collect right at the seat of the main valve of the reservoir gas tank, where they cause serious corrosion and frequently blockage of the main valve. Such clogged gas tanks with high pressures of hazardous gases present serious safety and disposal issues. The simple pump/purge step mentioned above should thus never be forgotten.

For the theoretical work, a 2006 version of the Spartan computer program was used to determine the stability of Argon and Neon complexes with  $\text{BF}_2^{2+}$ . We used a cc-pVTZ basis set with the B3LYP density functional [34–37] in order to calculate the equilibrium

geometry at the ground state. The charge and multiplicity (doublet for an odd number of electrons and singlet for an even number) had to be adjusted to suit the characteristics of each compound in the reaction. The computed energetics are given in terms of electron volts (eV) and refer to total energies at 0 K. A test calculation for the dication  $\text{ArBF}_2^{2+}$  indicated that the basis set superposition error at our level of theory is in the order of 0.02 eV. This number is at the border of the precision of the method, therefore in the following the possible basis set superposition error is not accounted for. Frequency analysis at the same level of theory was performed for all optimized structures, in order to assign stationary points on the potential-energy surface as genuine minima or transition structures, as well as to calculate zero-point vibrational energies (ZPVEs). All results were further checked by an independent optimization at the same level of theory (B3LYP/cc-pVTZ) using the Gaussian 09 program [38] and the results listed below refer to these values.

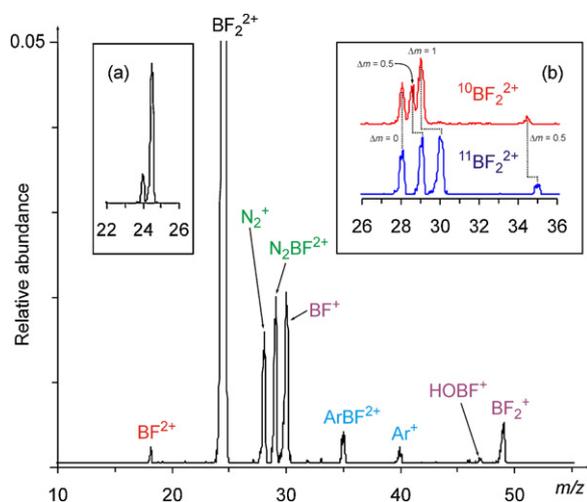
**Scholarly implementation.** The theoretical part of this work was performed within an undergraduate course in theoretical chemistry at the Manhattan College under the supervision of JFC in spring 2010. This course is a senior level requirement for all Chemistry and Biochemistry majors, and is a popular elective with Chemical Engineering majors. Our task is to cover chemical bonding by doing calculations on new materials and molecular systems as presented in the current literature. We stress molecular mechanics, semi-empirical, and ab initio methods with a strong emphasis on density functional theory, through hands on use of standard quantum chemistry programs such as Gaussian, Orca, and Spartan. Past class projects have included calculating UV–Vis spectra for photogray optical lenses, predicting the spectra of blue dyes of archeological interest, a mechanism of DNA intercalation, and the structure and bonding of proposed novel organic compounds recently detected in deep space. After being taught basics in quantum chemistry and ab initio computations, the students received different parts of the  $\text{BF}_n^{+/2+} + \text{Ne}(\text{Ar})$  systems as tasks for performing independent ab initio calculations, including the detailed analysis of the results. The complete set of results was then compiled by the entire course, discussed in detail, and summarized in a first draft of the paper. The results of the students were carefully controlled by JFC and afterwards JR checked all data by fully independent calculations at the same level of theory.

### 3. Results and discussion

The experiments on the  $\text{BF}_n^{+/2+}/\text{Ar}$  system were initiated by a suggestion of the supervisor of the theoretical course (JFC), who coordinated the theoretical study executed in parallel to the experiments. In the following, we first describe the experimental findings, followed by a summary of the results of the computational studies.

#### 3.1. Experimental results

Not unexpectedly, the experiments with boron trifluoride are harmful to the inlet system and the mass spectrometric instrumentation. Thus, even with traces of moisture  $\text{BF}_3$  liberates corrosive hydrogen fluoride, but even more so  $\text{BF}_3$  itself is a strong Lewis acid and thus highly corrosive. In practice, this manifest in pale, hygroscopic deposits in all parts of the inlet system of the mass spectrometer and the transfer lines, which are to be treated with caution because of the possible generation of gaseous HF. Likewise, the components of high vacuum manifold suffer in the presence of  $\text{BF}_3$  as manifested by a continuous decrease of the performance of the filament used in electron ionization as well as an unstable

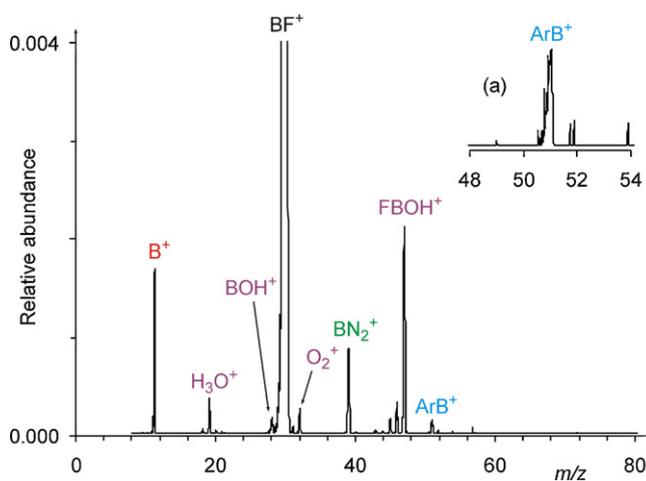
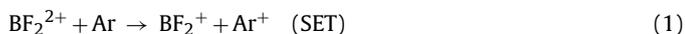


**Fig. 1.** Reaction of the mass-selected  $\text{BF}_2^{2+}$  dication generated by dissociative electron ionization of boron trifluoride with 0.1 mTorr argon at a nominal collision energy of 0 eV; in addition to argon as the desired reactant, some nitrogen from purging the  $\text{BF}_3$  was present in the high-vacuum system. The abundance scale is given relative to the precursor ion (1.00). Inset (a) is a neutral-gain scan of the mass regions around  $\text{BF}_2^{2+}$  with a mass gain of  $\Delta m = +10.5$  (i.e., addition of Ar and loss of F for a dication), which shows the expected isotope pattern of boron. In such a neutral-gain (or loss) scan, the first and the second quadrupoles of the instrument are scanned simultaneously with a fixed offset ( $\Delta m$ ) such that only those ions whose reactions are associated with a certain mass difference reach the detector [12,25]. Inset (b) show the peaks from  $m/z$  26–36 obtained when mass-selecting  $^{11}\text{BF}_2^{2+}$  (blue) and  $^{10}\text{BF}_2^{2+}$  (red), respectively.

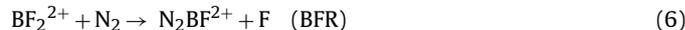
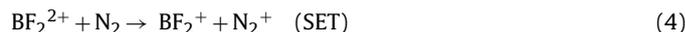
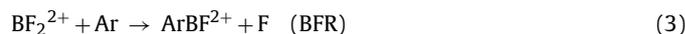
response of the high-vacuum ion gauge for pressure measurement. These harmful effects could be reduced by a parallel purging of the source manifold with nitrogen, which is in turn associated with some diffusion of nitrogen gas from the source region to the interaction region used to study ion/molecule reactions. Hence, the reactions with argon reported below also include reactions with molecular nitrogen. Further, due to the obviously harmful effect of  $\text{BF}_3$  on the instrumentation, the overall measuring time was restricted to a few hours, and hence more sophisticated experiments possible in our set-up (e.g., calibrated rate constants, detailed energy dependences, etc.) [12,23,30,33] were omitted for the sake of the equipment [39].

Electron ionization of  $\text{BF}_3$  in the positive ion mode provides the cations  $\text{BF}_n^+$  ( $n=0-3$ ) [40–45] and – about two orders of magnitude less abundant – the dications  $\text{BF}_n^{2+}$  ( $n=0-2$ ) [46]. Using MS/MS techniques in our multipole device [23,24], these species were probed with respect to their quasi-thermal reactivity with argon. Due to the use of nitrogen as a purging gas in the ion source, the reactions with  $\text{N}_2$  were studied in parallel. Note that argon and nitrogen are quite similar reactants in several respects [12,13]. For example, the ionization energy  $IE(\text{Ar}) = 15.759$  eV almost matches  $IE(\text{N}_2) = 15.581$  eV, and also the proton affinities  $PA(\text{Ar}) = 3.83$  eV and  $PA(\text{N}_2) = 5.12$  eV do not differ too largely [47]. Therefore, the parallel information about the reactivity of the  $\text{BF}_n^{+}/^{2+}$  cations with Ar as well as  $\text{N}_2$  can in fact be regarded as a useful complement.

As an example for the reactivity of the dicationic species, Fig. 1 shows the mass spectrum obtained for the  $\text{BF}_2^{2+}$  dication, where the experiments shown in the insets (a) and (b) verify the assignments made below. The major ionic products with argon can be summarized in Eqs. (1)–(3) and similarly, the reactions (4)–(6) occur with nitrogen; minor reactions due to residual water are discussed further below.



**Fig. 2.** Reaction of the mass-selected  $\text{BF}^+$  monocation generated by dissociative electron ionization of boron trifluoride with 0.1 mTorr argon at a nominal collision energy of 0 eV; in addition, residual nitrogen from purging the  $\text{BF}_3$  was present in the high-vacuum system. The abundance scale is given relative to the precursor ion (1.00). Inset (a) show the peaks at  $m/z$  51 at expanded scales.



Reactions (1)–(7) can be ascribed to (i) single electron transfer (SET) between the highly electrophilic dication and the neutral reagent (reactions (1) and (4)), likewise (ii) dissociative electron transfer (DET) can occur due to the large exothermicities of most charge-separation reactions [48] (reactions (2) and (5)), and (iii) bond-forming reactions (BFR) affording new gaseous dications with maintenance of the two-fold charge [3,4,49] (reactions (3) and (6)). In addition, a small amount of collision-induced dissociation (CID) and/or metastable ion decay (MI) is observed (reaction (7)). Observation of the latter process highlights the excess energy deposited in the cations formed upon electron ionization, because the fragmentation of  $\text{BF}_2^{2+}$  via loss of fluorine is an endothermic process [40].

Much weaker in abundance, but still significant were bond-forming reactions of the  $\text{BF}^+$  monocation, monitored in a separate experiment, which lead to the species  $\text{BN}_2^+$  and  $\text{ArB}^+$  in conjunction with loss of a fluorine atom (Fig. 2). In 1999, Koskinen and Cooks reported the formation of  $\text{BRg}^+$  monocations ( $\text{Rg} = \text{Ar}, \text{Kr}, \text{Xe}$ ) in collisions of  $\text{BBr}^+$  with rare gases as a very similar process [16]. Further, the corresponding reactivity is observed for the nitrogen gas present in the collision region and leads to  $\text{BN}_2^+$  cation as one of the major products. Note, however, that the overall reaction efficiency is low as demonstrated by reference to the abundance scale in which the sum of the product ions comprises less than 1% of the total ion signal.

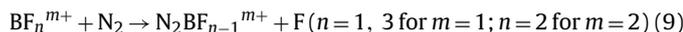
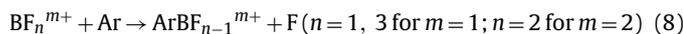
Although with a low efficiency, another bond-forming reaction was found in the reaction of argon with the molecular ion  $\text{BF}_3^+$  which leads to an ion with  $m/z$  89 which corresponds to  $\text{ArBF}_2^+$  (Fig. 3); for the  $^{10}\text{B}$  isotope of  $\text{BF}_3^+$  this product shifts to  $m/z$  88, as expected. The major product ion corresponds to  $\text{BF}_2^+$  as the product of the dissociation of metastable  $\text{BF}_3^+$  ions as well as some amount of collisional activation of  $\text{BF}_3^+$  to afford  $\text{BF}_2^+$  in the presence of the neutral collision partners. Further, small amounts of electron transfer are observed, which is consistent with  $IE(\text{BF}_3) = (15.7 \pm 0.3)$  eV [47] compared to  $IE(\text{Ar}) = 15.759$  eV and  $IE(\text{N}_2) = 15.581$  eV. Again,

**Table 1**Summary of the observed reactions of  $\text{BF}_n^{+/2+}$  mono- and dications with neutral argon and nitrogen at quasi-thermal conditions.<sup>a</sup>

	$\text{N}_2^+$	$\text{N}_2\text{BF}_2^{2+}$	$\text{BF}_2^{2+}$	$\text{ArBF}_2^{2+}$	$\text{BN}_2^+$	$\text{Ar}^+$	$\text{ArB}^+$	$\text{N}_2\text{BF}_2^+$	$\text{ArBF}_2^+$	Others <sup>b</sup>
$\text{B}^+$										No reaction
$\text{BF}^+$					1		<1			$\text{B}^+$ (2), $\text{HOBF}^+$ (2)
$\text{BF}_2^+$										$\text{HOBF}^+$ (3)
$\text{BF}_3^+$	5							22	2	$\text{BF}_2^+$ (130)
$\text{BF}_2^{2+}$	2		1							$\text{B}^+$ (<1)
$\text{BF}_2^{2+}$	16	19	20	4						$\text{BF}_2^{2+}$ (2), $\text{BF}_2^+$ (6)

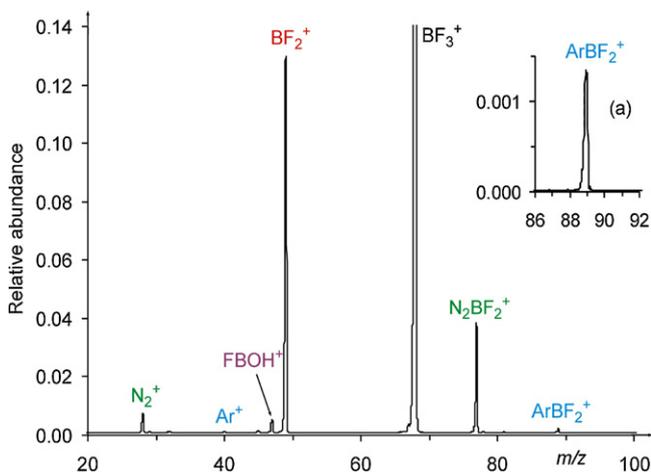
<sup>a</sup> Taken under identical conditions with the mass-selected precursor ion equal to 1000.<sup>b</sup> The oxygen-containing products are due to reactions with traces of water present in the background of the instrument.

nitrogen undergoes the analogous reaction to afford a  $\text{N}_2\text{BF}_2^+$  cation.



The results obtained for the other  $\text{BF}_n^{+/2+}$  cations are summarized in Table 1, where the abundances of the product ions are given relative to the precursor ion. Although less efficient, bond-forming reactions with argon are observed for the monocations  $\text{BF}^+$  and  $\text{BF}_3^+$  and the dication  $\text{BF}_2^{2+}$ , and in all cases these reactions can be described as a displacement of a fluorine atom by argon (reaction (8)). These results are complemented by the same type of reactivity observed with dinitrogen (reaction (9)). In the case of the  $\text{BF}^+$  monocation, the low reactivity suggests that the bond-forming product might also be due to an electronically excited state of this diatomic cation.

While the B–F bond in general is a rather strong chemical bond, consideration of the electronic structure of the precursor ions involved provides a straightforward rationale for the facile loss of atomic fluorine. Thus, the molecular ion  $\text{BF}_3^+$  is an open-shell compound for which the loss of atomic fluorine leads to the closed-shell species  $\text{BF}_2^+$  which is a linear molecule isoelectronic to  $\text{CO}_2$ . Similarly, the  $\text{BF}_2^{2+}$  dication is an open-shell species from which loss of atomic fluorine leads to the closed-shell compound  $\text{BF}^+$ , which is a diatomic dication with an extraordinary deep potential-energy well [46]. Likewise,  $\text{BF}^+$  is a radical cation, whereas all other, non-reactive species are formal closed-shell species.

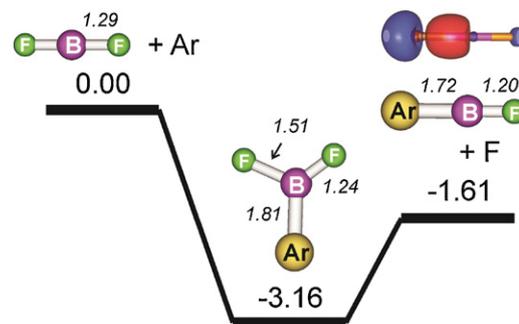


**Fig. 3.** Reaction of the mass-selected  $\text{BF}_3^+$  monocation generated by electron ionization of boron trifluoride with 0.1 mTorr argon at a nominal collision energy of 0 eV; in addition, residual nitrogen from purging the  $\text{BF}_3$  was present in the high-vacuum system. The abundance scale is given relative to the precursor ion (1.00). Inset (a) show the peaks at  $m/z$  89 at expanded scales.

### 3.2. Theoretical calculations

With respect to the experimental results, the theoretical survey focused on the reactions of argon with the  $\text{BF}_3^+$  monocation and the  $\text{BF}_2^{2+}$  dication (Table 2). Fully consistent with the measurement, reaction (8) is found to be 1.61 eV exothermic for  $\text{BF}_2^{2+}$  as a precursor (Fig. 4). Notable is also the binding energy of argon in the intermediate  $\text{ArBF}_2^{2+}$  which amounts to 3.16 eV and hence reaches the strength of typical covalent bonds. In comparison, the B–F bond in  $\text{ArBF}_2^{2+}$  is much weaker (1.55 eV), hence accounting for the formation of  $\text{ArBF}_2^{2+}$  as the ionic product. In the  $\text{ArBF}_2^{2+}$  intermediate, one B–F bond is slightly shortened with respect to the  $\text{BF}_2^{2+}$  reactant (see Fig. 4), whereas the other B–F bond is significantly elongated to 1.51 Å. The bond distance between boron and argon is 1.81 Å. A qualitative assessment of the bonding situation can be obtained from the Mulliken bonding analysis. It suggests that the Ar–B bond is associated with 0.35 shared electrons, whereas the B–F bonds share 0.52 and 0.26 electrons, respectively. The latter value corresponds to the longer bond and on the corresponding fluorine atom is also mostly localized the unpaired electron (0.87 e). The subsequent elimination of the fluorine atom leads to a shortening of both remaining bonds, hence the argon–boron bond length amounts to 1.72 Å and the boron–fluorine distance shrink to 1.20 Å. The bonding analysis leads to the values of 0.40 and 0.57 shared electron in these bonds, respectively.

The reaction between  $\text{BF}_3^+$  monocation and argon leading to the second observed argon-containing ion,  $\text{ArBF}_2^+$ , is predicted to be endothermic by 0.46 eV. This finding is consistent with the low yield of the bond-forming product and the prevalence of the competing fragmentation of  $\text{BF}_3^+$  into  $\text{BF}_2^+ + \text{F}$  (Figs. 2 and 5). The occurrence of the endothermic process  $\text{Ar} + \text{BF}_3^+ \rightarrow \text{ArBF}_2^+ + \text{F}$  is attributed to the excess energy deposited in the precursor ions upon electron ionization. The  $[\text{ArBF}_3]^+$  intermediate does not contain an Ar–B bond as it was found in the previous case, but it can be rather considered as a van der Waals complex, in which argon interacts with fluorine atoms (Fig. 5). Nevertheless, in the



**Fig. 4.** B3LYP/cc-pVTZ potential energy surface for the reaction between  $\text{BF}_2^{2+}$  and Ar. Relative energies are given in eV and the bond lengths (in italics) are in angstroms. The orbital picture shows the binding orbital for the Ar–B bond.

**Table 2**  
Computed energies (all in eV) of the reaction between  $\text{BF}_n^{+/2+}$  cations and neutral argon.

	$E_{\text{el}}$	ZPVE	$E_{0\text{K}}$	Derived quantities
F	-2714.69	0	-2714.69	
Ar	-14 355.62	0	-14 355.62	
$\text{BF}^+$	3382.65	0.10	3382.55	
$\text{ArB}^+$	-15 018.49	0.02	-15 018.47	$\Delta_f H_0(8, \text{BF}^+) = 5.01 \text{ eV}^a$
$\text{BF}_2^+$	-6104.71	0.25	-6104.46	$D_0(\text{BF}_2^+ - \text{F}) = 7.23 \text{ eV}$
$\text{ArBF}_2^+$	-20 460.77	0.27	-20 460.50	$D_0(\text{Ar}-\text{BF}_2^+) = 0.42 \text{ eV}^a$
				$\Delta_f H_0(8, \text{BF}_3^+) = 0.46 \text{ eV}^b$
$\text{ArBF}^+$	-17 738.68	0.11	-17 738.56	$D_0(\text{ArBF}^+ - \text{F}) = 7.26 \text{ eV}$
				$\Delta_f H_0(8, \text{BF}_2^+) = 6.83 \text{ eV}^b$
$\text{BF}_2^{2+}$	-6078.79	0.11	-6078.68	$IE(\text{BF}_2^+) = 25.78 \text{ eV}$
$\text{ArBF}_2^{2+}$	-20 437.66	0.20	-20 437.46	$D_0(\text{Ar}-\text{BF}_2^{2+}) = 3.16 \text{ eV}$
				$IE(\text{ArBF}_2^+) = 23.04 \text{ eV}$
$\text{ArBF}^{2+}$	-17 721.41	0.19	-17 721.22	$D_0(\text{ArBF}^{2+} - \text{F}) = 1.55 \text{ eV}$
				$\Delta_f H_0(8, \text{BF}_2^{2+}) = -1.61 \text{ eV}^b$
$\text{BF}_3^+$	-3359.14	0.11	-3359.02	$D_0(\text{Ar}-\text{BF}_3^+) = 6.58 \text{ eV}$
$\text{BF}_3^+$	-8820.30	0.27	-8820.03	$D_0(\text{BF}_2^+ - \text{F}) = 0.88 \text{ eV}$
$\text{ArBF}_3^+$	-23 177.13	0.33	-23 176.80	$D_0(\text{Ar}-\text{BF}_3^+) = 1.16 \text{ eV}$

<sup>a</sup> A value of 0.46 eV has been reported in recent wave-function based ab initio studies [22].

<sup>b</sup> Computed enthalpy of reaction (8) for the reactant given in the bracket behind the comma.

**Table 3**  
Computed energies (all in eV) of the reaction between  $\text{BF}_n^{+/2+}$  cations and neutral neon.

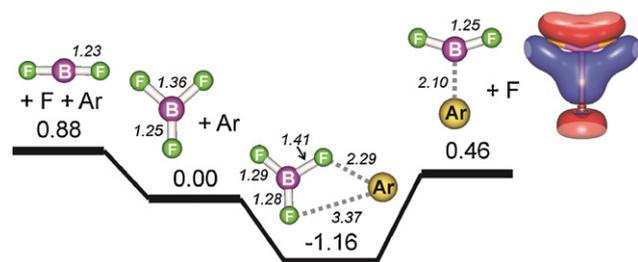
	$E_{\text{el}}$	ZPVE	$E_{0\text{K}}$	Derived quantities
Ne	-3509.23	0	-3509.23	
$\text{NeBF}_2^+$	-9614.08	0.26	-9613.82	$D_0(\text{Ne}-\text{BF}_2^+) = 0.12 \text{ eV}$
				$\Delta_f H_0(8_{\text{Ne}}, \text{BF}_3^+) = 0.75 \text{ eV}^a$
$\text{NeBF}^+$	-6892.07	0.12	-6891.95	$D_0(\text{NeBF}^+ - \text{F}) = 7.18 \text{ eV}$
				$\Delta_f H_0(8_{\text{Ne}}, \text{BF}_2^+) = 7.06 \text{ eV}^a$
$\text{NeBF}_2^{2+}$	-9589.41	0.21	-9589.20	$D_0(\text{Ne}-\text{BF}_2^{2+}) = 1.29 \text{ eV}$
				$IE(\text{NeBF}_2^+) = 24.62 \text{ eV}$
$\text{NeBF}^{2+}$	-6871.69	0.19	-6871.50	$D_0(\text{NeBF}^{2+} - \text{F}) = 3.01 \text{ eV}$
				$\Delta_f H_0(8_{\text{Ne}}, \text{BF}_2^{2+}) = 1.72 \text{ eV}^a$
				$D_0(\text{Ne}-\text{BF}_2^+) = 3.25 \text{ eV}$
$\text{NeBF}_3^+$	-12 329.65	0.29	-12 329.35	$D_0(\text{Ne}-\text{BF}_3^+) = 0.10 \text{ eV}$

<sup>a</sup> Computed enthalpy of the analog of reaction (8) with neon for the reactant given in the bracket behind the comma.

course of the reaction, argon replaces one fluorine atom and forms a weak bond to boron. The argon–boron bond length amounts to 2.10 Å. The bonding analysis predicts that the boron–fluorine bonds are associated with 0.57 shared electron each, whereas the boron–argon bond has only 0.19 shared electrons.

Finally, the absence of bond-forming products in the reaction of  $\text{BF}_2^+$  with argon is fully supported by theory, which predicts the formation of the corresponding  $\text{ArBF}_2^+$  cation to be endothermic by almost 7 eV.

For comparison, we have also studied computationally the corresponding reactions of neon (Table 3); for some isomeric  $\text{FRgBF}^+$  ions, also see Ref. [22]. For this lighter rare gas, all bond-forming processes are clearly endothermic, such that any reactivity possibly observed could only arise from contributions of electronically excited states of the precursor ions formed upon electron ionization.



**Fig. 5.** B3LYP/cc-pVTZ potential energy surface for the reaction between  $\text{BF}_3^+$  and Ar. Relative energies are given in eV and the bond lengths (in italics) are in angstroms. The orbital picture shows the binding orbital for the Ar–B bond.

In comparison, the bond-forming channels with the superelectrophilic  $\text{BF}_n^{+/2+}$  cations are much more pronounced for argon than for neon. However, both rare gases share a trend in that the first half of the reaction involves a transient adduct from which ‘cooling’ by loss of atomic fluorine eventually leads to the substitution products.

#### 4. Conclusions

Among the  $\text{BF}_n^{+/2+}$  cations accessible by electron ionization of neutral  $\text{BF}_3$ , the dication  $\text{BF}_2^{2+}$  is able to promote the formation of a rare-gas compound  $\text{ArBF}_2^+$  in the reaction with argon. Theory predicts this process to start with the formation of an  $\text{ArBF}_2^{2+}$  complex having a binding energy of 3.16 eV, which is in the order of magnitude of typical covalent bonds. The reaction is completed by loss of a neutral fluorine atom resulting in a net exchange for fluorine by argon with an overall exothermicity of 1.61 eV. These observations suggest  $\text{BF}_2^{2+}$  as one of the strongest and most reactive electrophiles in the gas phase. Similar processes with Ar–B bond formation, though less efficiently, occur for the monocations  $\text{BF}^+$  and  $\text{BF}_3^+$ , which are both open-shell species, whereas the closed-shell ions like  $\text{BF}_2^+$ ,  $\text{BF}_2^{2+}$  are unreactive towards argon. While nitrogen reacts in a manner very similar to argon, theory predicts that rare-gas species are not likely to be formed with neon as a reagent.

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