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Gas-Phase Ion Chemistry of BF_3/NH_3 Mixtures

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The gas-phase ion chemistry of BF_3/NH_3 mixtures was investigated by the joint application of mass-spectrometric techniques and theoretical methods. The addition of BF_2^+ to NH_3 led to the first observation of $[BF_2,NH_3]^+$ and $[BF,NH_2]^+$ ions. Diamidoboron cation $B(NH_2)_2^+$ was also detected. Consistent with collisionally activated dissociation (CAD) mass spectrometric results, theoretical calculations performed at the B3LYP and CCSD(T) levels identified the $F_2B{-}NH_3^+$, $FB{-}NH_2^+$, and $NH_2{-}B{-}NH_2^+$ ions as the most stable isomers on the corresponding potential energy surfaces. The $F_2B{-}NH_3^+$ ion represents the protonated form of aminodifluoroborane, BF_2NH_2, and consequently behaves as a Brønsted acid under FT-ICR conditions. The $FBNH_2^+$ ion is able to add Lewis bases such as water, ammonia, and hydrazoic acid. These species, containing the BN moiety, may represent new promising projectile ions in the boron nitride deposition techniques involving high-energy ion beams.

Introduction

Boron−nitrogen containing compounds have been of interest to chemists for nearly two centuries. The classical donor−acceptor complex BF_3NH_3 was the first known coordination compound of any element, synthesized in 1809 by Gay-Lussac[1] and used by Lewis to illustrate the theory of the donor−acceptor bond.[2]

Following its discovery, a large number of experimental and theoretical studies were conducted on its structural characterization, but only in 1991 was it detected in the gas phase by Legon and Warner.[3]

Despite the enormous interest witnessed by numerous publications on the neutral complex,[4] relevant data on the gas-phase ion chemistry of BF_3/NH_3 mixtures are relatively scant. This state of affairs is even more surprising considering that gaseous mixtures of BF_3 and NH_3 have received great attention in past decades for their use in boron nitride (BN) film deposition. In particular, boron trifluoride and ammonia are commonly used as reactants in boron nitride chemical and physical vapor depositions.[5]

Recently we reported the first experimental observation of gaseous $[BF_nN_xH_{n-1}]^+$ ($n = 1, 2$; $x = 1, 3$) ions obtained from the gas-phase ionization of BF_3/HN_3 mixtures.[6] In this study we extended our investigation to the gas-phase ion chemistry of BF_3/NH_3 mixtures. The structures and reactivity of the $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) ions formed, never previously experimentally detected but only theoretically investigated,[7,8] was studied by the joint application of mass spectrometric and ab initio theoretical methods.

Also, in this case, the ionic products obtained contain the BN moiety and hence could prove, at least in principle, excellent projectile ions in boron nitride deposition techniques. Furthermore, the knowledge of the formation and decomposition mechanisms of ionic compounds in the B−N−F−H system are fundamental for the comprehension of the processes involved in boron nitride deposition.

Experimental Section

All the gases used were purchased from Matheson Gas Products Inc. with a stated purity of 99.9 mol %.

Mass Spectrometric Experiments. Triple quadrupole mass spectrometric experiments were performed with a TSQ 700 instrument from Thermofinnigan Ltd. The ions generated in the chemical ionization (CI) source were driven into the collision cell, actually an rf-only hexapole, containing the neutral reagent. The collisionally activated dissociation (CAD) spectra were recorded utilizing Ar as the target gas at pressures up to 1×10^{-5} Torr and at nominal collision energies ranging from 0 to 50 eV (laboratory frame). The charged products were analyzed with the third quadrupole, scanned at a frequency of 150 amu s^{-1}.

Fourier transform ion cyclotron resonance (FT-ICR) measurements were performed using an Apex TM 47e spectrometer from Bruker Spectrospin AG equipped with an external ion source operating in the CI mode. The ions, generated in the external source, were transferred into the resonance cell, isolated by broad-band and "single-shot" ejection pulses and thermalized by collisions with Ar introduced in the cell by a pulsed valve. The pressure of the neutral reactant introduced in the cell, ranging from 1×10^{-8} to 1×10^{-7} Torr, was measured by a Bayard-Alpert ionization gauge whose reading was corrected for the relative sensitivity to the various gases used according to standard procedures.[9]

Computational Methods. Density functional theory, using the hybrid[10] B3LYP functional,[11] was used to optimize the geometry of relevant species and evaluate their vibrational frequencies. Although it is well-known that density functional methods using nonhybrid functionals sometimes tend to over-

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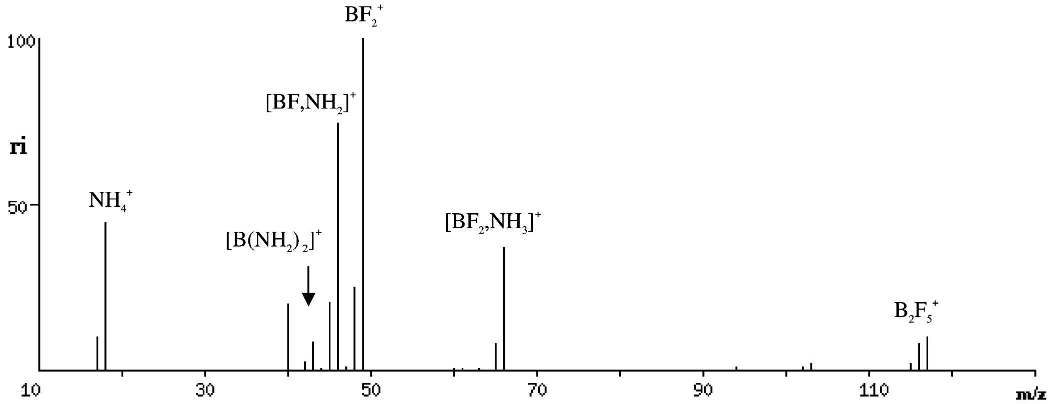


Figure 1. BF_3/CI spectrum of ammonia.

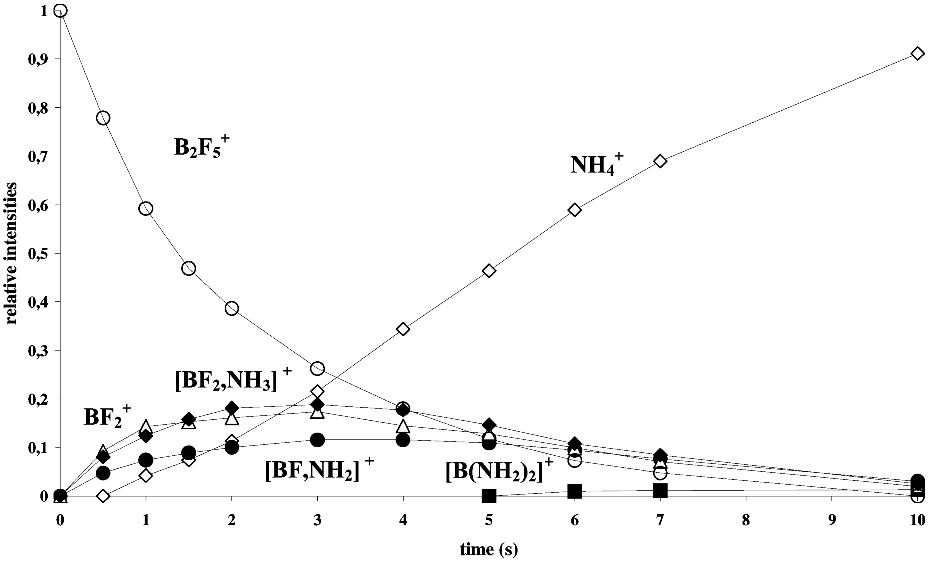


Figure 2. Time profiles of the ionic intensities of the products obtained from the reaction of $B_2F_5^+$ ions with NH_3.

estimate bond lengths,[12] hybrid functionals such as B3LYP usually provide geometric parameters in excellent agreement with experiment.[13] Single point energy calculations at the optimized geometries were performed using the coupled-cluster single and double excitation method[14] with a perturbational estimate of the triple excitation [CCSD(T)] approach,[15] in order to include extensively correlated contributions.[16] Transition states were located using the synchronous transit-guided quasi-Newton method due to Schlegel and co-workers.[17] The 6-311+G(2d) basis set was used.[18] Zero point energy corrections evaluated at the B3LYP/6-311+G(2d) level were added to CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational, and vibrational contributions. The absolute entropies were calculated by standard statistical-mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311+G(2d) optimized geometries. All calculations were performed using Gaussian 03.[19]

Results

Figure 1 displays the triple quadrupole (TQ) BF_3/CI mass spectrum of ammonia. A similar spectrum was observed in the CI source of the FT-ICR mass spectrometer. The spectrum shows the peaks at *m*/*z* 48/49 and *m*/*z* 115, 116, and 117 characteristic of the self-CI mass spectrum of BF_3 and corresponding to the BF_2^+ and $B_2F_5^+$ ions, respectively. The addition of a small amount of NH_3 to the CI plasma leads to the appearance of the ionic species at *m*/*z* 65/66, *m*/*z* 45/46, and *m*/*z* 42/43 formally corresponding to the $[BF_2,NH_3]^+$ $[BF,NH_2]^+$, and $[B(NH_2)_2]^+$ ions, respectively. The elemental composition was confirmed by FT-ICR high accuracy *m*/*z* measurements. The CI spectrum also shows the NH_3^+ and NH_4^+ ions at *m*/*z* 17 and *m*/*z* 18 generated by electron and proton transfer processes.

To identify the formation pathway of these ionic species, the possible ionic precursors, BF_2^+ or $B_2F_5^+$, were isolated in the FT-ICR cell and allowed to react with NH_3.

As evident from Figure 2 the reaction of the $B_2F_5^+$ ions with neutral NH_3 leads to the formation of the $[BF_2,NH_3]^+$ adduct at *m*/*z* 65/66 and of the fragment ions $[BF,NH_2]^+$ at *m*/*z* 45/46.

At longer reaction times the diamidoboron cation, $[B(NH_2)_2]^+$, of *m*/*z* 42/43 appears. This species arises from the loss of an HF molecule from the $[BF,NH_2,NH_3]^+$ adduct generated by the addition of an NH_3 molecule to $[BF,NH_2]^+$ as demonstrated by FT-ICR experiments where the $[BF_2,NH_2]^+$ ions were isolated in the presence of ammonia (vide infra).

The reaction of BF_2^+ ions with ammonia leads only to the observation of the $[BF,NH_2]^+$ fragment ion owing to the inefficient thermalization of the $[BF_2,NH_3]^+$ adduct in the low-pressure conditions of the ICR cell. In all the FT-ICR experiments high intensities of the NH_4^+ ions appear, due to a fast proton transfer from $[BF_2,NH_3]^+$ to the highly basic ammonia.

Structural Characterization of the $[BF_nNH_{n+1}]^+$ ($n = 1$, 2) and $[B(NH_2)_2]^+$ Ions. Collisionally activated dissociation

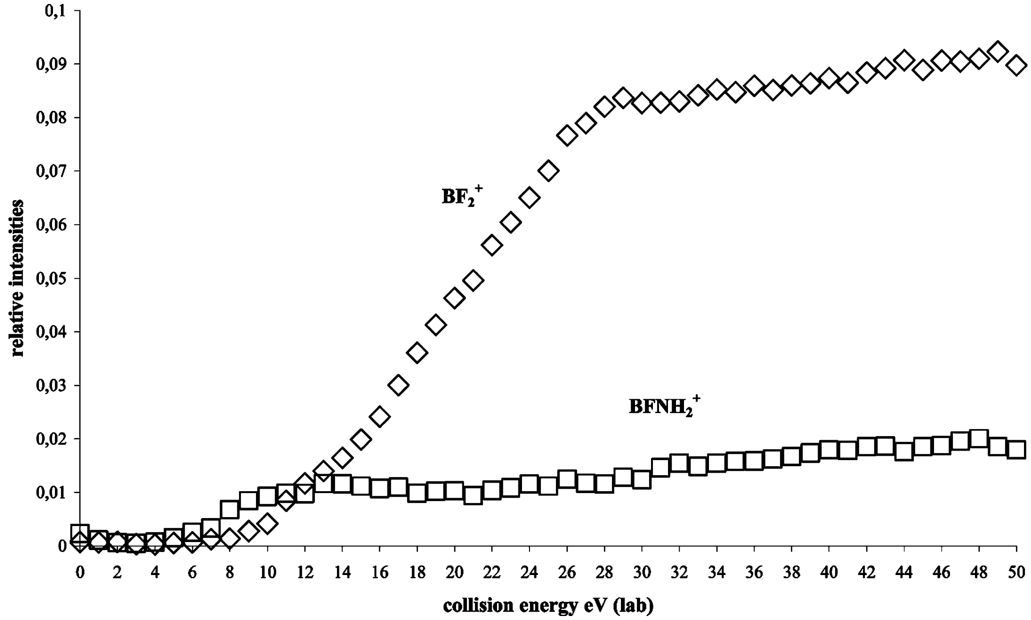


Figure 3. Energy-resolved TQ/CAD spectrum of the $[^{11}BF_2,NH_3]^+$ ions.

(CAD) mass spectrometry has been used to obtain structural information on the ionic species observed.

The addition of NH_3 to BF_2^+ forms isomers **1**. At least in principle, the existence of an additional protomer, **2**, arising from **1** through a proton shift on a fluorine atom of the BF_2 moiety can be postulated.

$F_2B{-}NH_3^+$ $HF{-}BF{-}NH_2^+$
1 **2**

The energy-resolved CAD spectrum of $[^{11}BF_2,NH_3]^+$ recorded at nominal collision energies ranging from 0 to 50 eV (laboratory frame) is reported in Figure 3.

The spectrum shows that the dissociation chemistry of the $[^{11}BF_2,NH_3]^+$ ions is dominated by the loss of the NH_3 molecule leading to the $^{11}BF_2^+$ fragment, which accounts for 90% of the whole ionic pattern at a collision energy of 50 eV. The formation of a $[^{11}BF,NH_2]^+$ ion, through the loss of an HF molecule, is the easier fragmentation channel, appearing at a collision energy of ca. 6 eV, slightly lower than that required for the loss of NH_3. The mass attribution of these fragments was confirmed by the shift of one *m*/*z* unit observed in the CAD spectrum of the corresponding $[^{10}BF_2,NH_3]^+$ ions.

As for the structure of the $[BF,NH_2]^+$ ions, considering that they are generated by the loss of the HF molecule from the $[BF_2,NH_3]^+$ adduct, we can hypothesize the existence of two different isomers, **3** and **4**. The $FBNH_2^+$ isomer **3** could be generated by the loss of the HF molecule from **2**, whereas the $HFBNH^+$ isomer could derive from **3** through a proton shift on a fluorine atom of the BF moiety.

$FB{-}NH_2^+$ $HF{-}B{-}NH^+$
3 **4**

The energy-resolved CAD spectrum of the $[^{11}BF_2,NH]^+$ ions recorded at nominal collision energies ranging from 0 to 60 eV is reported in Figure 4. The spectrum shows two main fragmentation channels leading to the $^{11}BF^+$ fragment at *m*/*z* 30 and to the $^{11}BNH_2^+$ fragment at *m*/*z* 27 corresponding to the loss of the NH_2 moiety and of a fluorine atom, respectively. A minor fragmentation channel leads to the formation of the BFH^+ ions at *m*/*z* 31. All these fragmentations require collision energies above 15 eV.

The energy-resolved CAD spectrum of the $[^{11}B(NH_2)_2]^+$ ions recorded at nominal collision energies ranging from 0 to 50 eV is reported in Figure 5. The spectrum shows the dissociation into the $^{11}BNH_2^+$ ion generated by the loss of the NH_2 moiety that appears at a collision energy of about 16 eV.

Reactivity of $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) Ions. The reactivity of $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) ions was investigated by FT-ICR mass spectrometry. The ions formed in the external CI ion source, transferred to the ICR cell and isolated after collisional thermalization by Ar, were allowed to react with selected nucleophiles introduced into the resonance cell. Table 1 reports the proton affinities (PA) and the ionization potentials (IP) of the nucleophiles used[20−22] and the reaction products observed.

The $[BF_2,NH_3]^+$ ions react by proton transfer with nucleophiles characterized at least by a PA value of 180.7 kcal mol^{-1}. Considering that no proton transfer was observed with H_2O, it is reasonable to assume that the gas-phase proton affinity of aminodifluoroborane, BF_2NH_2, can be positioned between the PA of H_2O (165.0 kcal mol^{-1}) and the PA of HN_3 (180.7 kcal mol^{-1}).

The $[BF,NH_2]^+$ ions react by charge transfer with molecules characterized by an IP of at least 11.18 eV.

In the FT-ICR experiments the observation of protonated products cannot be attributed unequivocally to the protonating ability of this ion since they may derive from self-protonation reactions involving the radical cations formed by charge transfer. Furthermore, an interesting reactivity of the $[BF,NH_2]^+$ ions is the nucleophilic attack on the electron-deficient boron atom by Lewis bases such as water, ammonia, and hydrazoic acid. The addition of H_2O and NH_3 is followed by the loss of an HF molecule leading to the $[NH_2BOH]^+$ and $[B(NH_2)_2]^+$ ions, respectively. The product obtained in the reaction with ammonia confirms the postulated mechanism of formation of the diammidoboron cation observed in the CI spectra. Figure 6 reports the time profile of the ionic intensities for the reaction between the $[BF,NH_2]^+$ ion and HN_3. The addition of hydrazoic acid is followed by the loss of a N_2 molecule leading to the $[NH_2,BF,NH]^+$ ions at *m*/*z* 60/61.

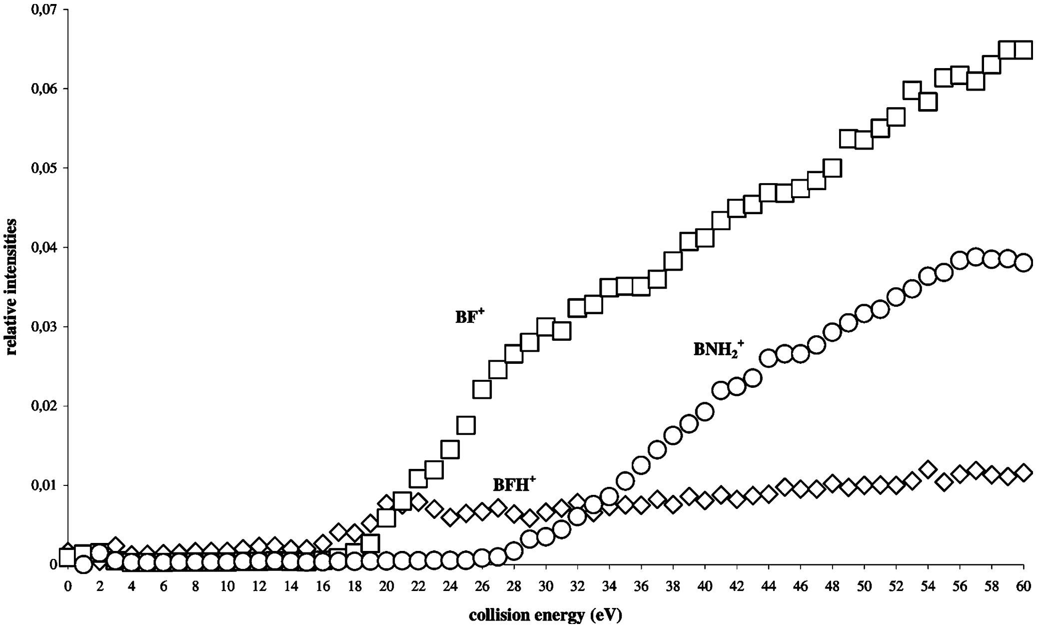


Figure 4. Energy-resolved TQ/CAD spectrum of the $[^{11}BF,NH_2]^+$ ions.

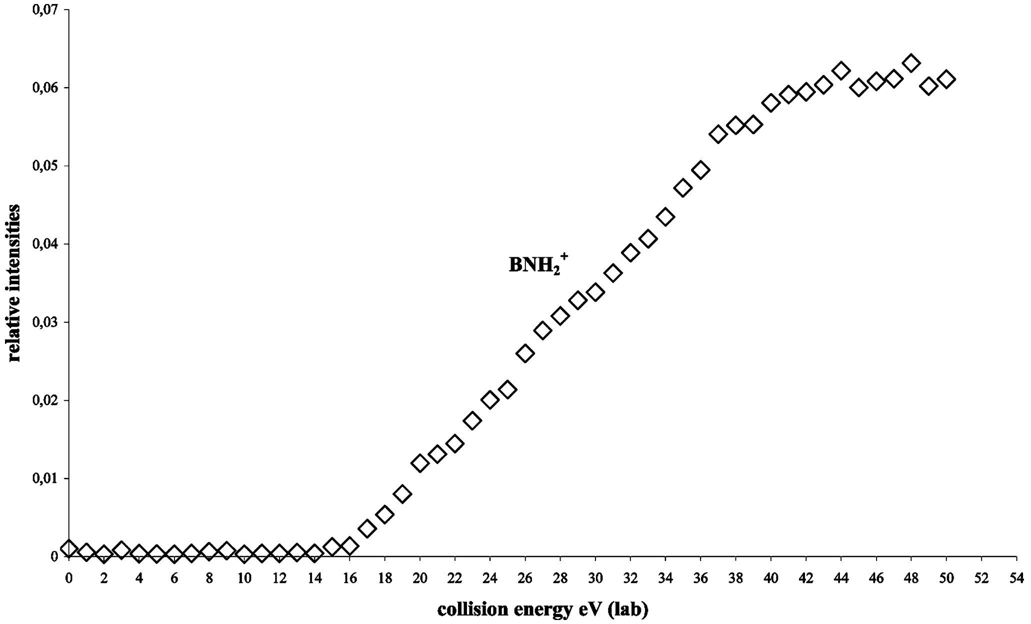


Figure 5. Energy-resolved TQ/CAD spectrum of the $[^{11}B(NH_2)_2]^+$ ions.

TABLE 1: FT-ICR Reactivity of $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) Ions

nucleophile	PA (kcal mol^{-1})	IP (eV)	products	
			$[BF_2,NH_3]^+$	$[BF,NH_2]^+$
CO	142.0	14.01	no reaction	no reaction
COS	150.2	11.18	no reaction	COS^+
H_2O	165.0	12.62	no reaction	$[NH_2BOH]^+$
HN_3	180.7	10.72	$H_2N_3^+$	$[NH_2,BF,NH]^+$/HN_3^+/$H_2N_3^+$
NH_3	204.0	10.07	NH_4^+	$[NH_2,B,NH_2]^+$/NH_3^+/NH_4^+

No reaction was observed with soft Lewis bases such as CO and COS.

The low intensity of the diamidoboron cation, $[B(NH_2)_2]^+$, does not permit the investigation of its reactivity by FT-ICR mass spectrometry.

Theoretical Calculations. To rationalize the structurally diagnostic results obtained by the CAD mass spectra, theoretical calculations were performed by using an approach based on density functional theory using the hybrid B3LYP functional. Additional calculations were carried out using the coupled-cluster single and double excitation method with a perturbational estimate of the triple excitation CCSD(T) approach. The optimized structures of the $[BF_2,NH_3]^+$, $[BF,NH_2]^+$, and $[B(NH_2)_2]^+$ ions are shown in Figure 7. The relative energies of these species and the exothermicity of their formation reactions, computed at 298 K at both B3LYP and CCSD(T) levels of theory, are reported in Table 2 together with the barrier heights for their isomerization processes. Table 2 also reports some selected dissociation reactions of the investigated ions.

The addition of BF_2^+ to NH_3 gives rise to two isomers, **1** and **2**, characterized by a different proton position. Isomer **1** resembles the connectivity of the BF_2^+ and NH_3 interacting species, whereas isomer **2** is characterized by a structure in which one proton of the NH_3 molecule is shifted on a fluorine

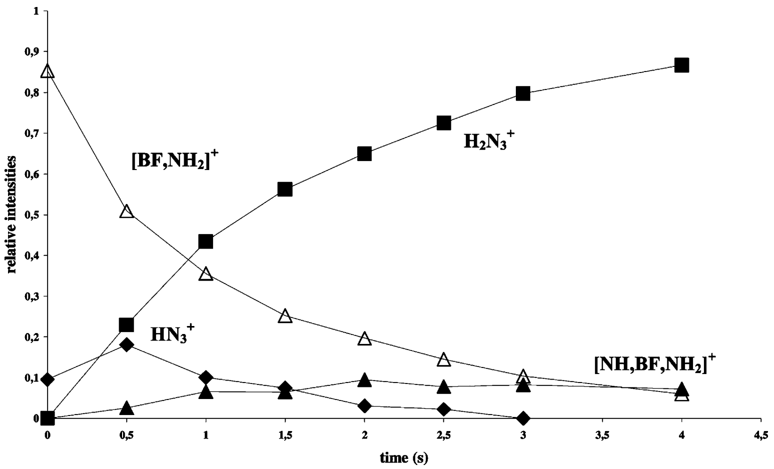


Figure 6. Time profiles of the ionic intensities of the products obtained from the reaction of $[BF,NH_2]^+$ ions with HN_3.

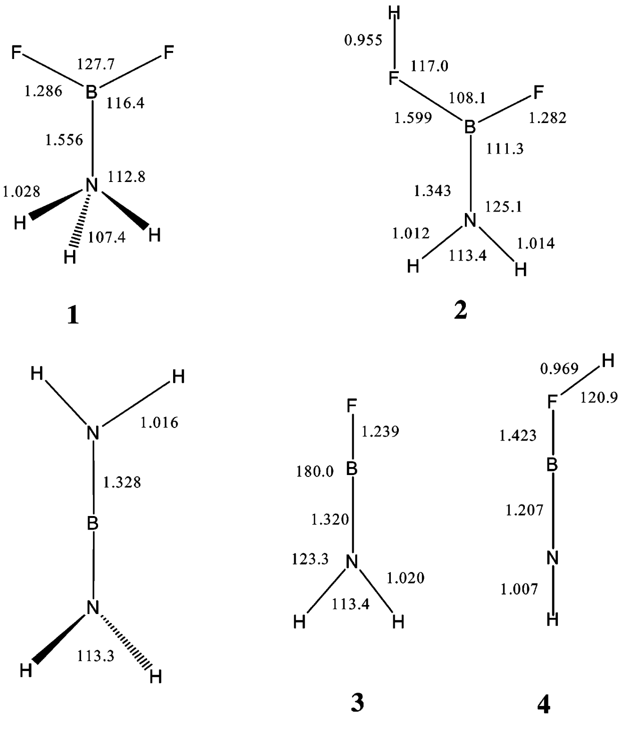


Figure 7. Optimized geometries of $[BF_2,NH_3]^+$, $[BF,NH_2]^+$, and $[B(NH_2)_2]^+$ ions. Bond lengths are in angstroms and bond angles in degrees.

atom of the BF_2 moiety. Species **1** is computed to be more stable than **2** by 46.9 (45.3) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory. The formation of **1** via the addition of BF_2^+ to NH_3 is exothermic by 92.7 (95.3) kcal mol^{-1}, whereas the same species is obtained from the reaction of $B_2F_5^+$ and NH_3 in a process exothermic by 66.1 (68.4) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory. The interconversion between ions **1** and **2** requires overcoming an activation barrier of 63.5 kcal mol^{-1} at the B3LYP level of theory (66.7 kcal mol^{-1} at the CCSD(T) level).

The loss of an HF molecule is the easiest dissociation channel of isomer **2**, requiring only 20.4 (24.4) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory.

The potential energy surface of the $[BF,NH_2]^+$ ions suggests the existence of two isomeric forms: the $FBNH_2^+$ ions, **3**, and the $HFBNH^+$ isomer, **4**, characterized by a structure in which one proton of the NH_2 group is shifted on a fluorine atom of the BF moiety. Isomer **3** is more stable than **4** by 87.4 (84.0) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory.

TABLE 2: Energy Changes (kcal mol^{-1}, 298 K) Computed at the B3LYP (CCSD(T)) Level of Theory for Selected Dissociation and Isomerization Reactions Relative to the System BF_3/NH_3

process	$\Delta H°$	barrier height
$BF_2^+ + NH_3 \rightarrow F_2BNH_3^+$	−92.7 (−95.3)	
$B_2F_5^+ + NH_3 \rightarrow F_2BNH_3^+ + BF_3$	−66.1 (−68.4)	
$F_2BNH_3^+ \rightarrow HFBFNH_2^+$	46.9 (45.3)	63.5 (66.7)
$HFBFNH_2^+ \rightarrow FBNH_2^+ + HF$	20.4 (24.4)	
$FBNH_2^+ + NH_3 \rightarrow B(NH_2)_2^+ + HF$	−19.6 (−20.9)	
$FBNH_2^+ \rightarrow HFBNH^+$	87.4 (84.0)	113.1 (113.7)
$FBNH_2^+ \rightarrow NH_2 + BF^+$	164.7 (162.7)	
$FBNH_2^+ \rightarrow F + BNH_2^+$	168.1 (164.6)	
$HFBNH^+ \rightarrow {}^3NH + HFB^+$	136.8 (123.3)	
$HFBNH^+ \rightarrow {}^3NH + FBH^+$	48.9 (46.1)	
$HFBNH^+ \rightarrow {}^1NH + HFB^+$	172.7 (159.2)	
$HFBNH^+ \rightarrow HF + {}^3BNH^+$	76.5 (77.5)	
$HFBNH^+ \rightarrow HF + {}^1BNH^+$	89.5 (89.4)	
$HFB^+ \rightarrow FBH^+$	−87.9 (−77.2)	24.2 (31.7)
$B(NH_2)_2^+ \rightarrow NH_2 + BNH_2^+$	161.4 (159.8)	

The isomerization of **3** to **4** requires overcoming an energy barrier of 113.1 kcal mol^{-1} at the B3LYP level of theory (113.7 kcal mol^{-1} at the CCSD(T) level).

The loss of NH_2 from $BFNH_2^+$ is endothermic by 164.7 kcal mol^{-1} at the B3LYP level (162.7 kcal mol^{-1} at the CCSD(T) level).

The easiest dissociation channel of the $HFBNH^+$ ions, **4**, is the spin-forbidden loss of NH in the triplet ground state, leading to the formation of the FBH^+ fragments, endothermic by 48.9 (46.1) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory. In this dissociation the HFB^+ fragment initially formed isomerizes to FBH^+ through a process exothermic by 87.9 (77.2) kcal mol^{-1} and having an energy barrier of 24.2 (31.7) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory.

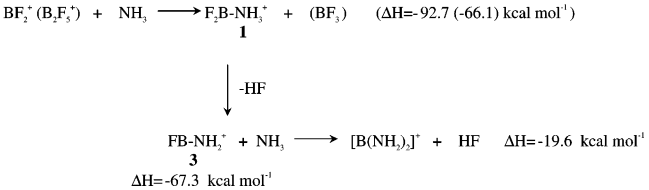
The diamidoboron cation, $[B(NH_2)_2]^+$, is formed from the addition of NH_3 to the $BFNH_2^+$ ions with the concomitant loss of an HF molecule in a process exothermic by 19.6 (20.9) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory.

The only fragmentation channel characteristic of this species is the dissociation into BNH_2^+ and NH_2, found to be endothermic by 161.4 (159.8) kcal mol^{-1} at the B3LYP (CCSD(T)) level of theory.

Discussion

The ionization of BF_3/NH_3 mixtures under typical mass spectrometric chemical ionization conditions leads to the first

SCHEME 1



observation of $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) ions according to Scheme 1. The addition of BF_2^+ to NH_3 leads to the $F_2B-NH_3^+$ ion, **1**, which, excited by the large exothermicity of its formation process, in the low-pressure regime of the FT-ICR cell, does not survive but generates the $FB-NH_2^+$ fragment ion through the loss of an HF molecule. In contrast, $F_2B-NH_3^+$ is observed in the reaction involving the $B_2F_5^+$ ions through a process less exothermic and more entropically favored by the loss of the BF_3 moiety. The $FB-NH_2^+$ fragment ion, **3**, may add a new molecule of ammonia to generate the diamidoboron cation, $B(NH_2)_2^+$, through the loss of HF.

The mutually supporting results obtained from the energy-resolved TQ/CAD mass spectra and theoretical calculations allow drawing a definitive conclusion on the structural characterization of these species.

For clarity only B3LYP values are reported; the corresponding CCSD(T) values are shown in Table 2.

At least in principle, the formation of the $HF-BF-NH^+$ isomer, **2**, less stable than **1** by 46.9 kcal mol^{-1}, cannot be ruled out. In fact, isomer **1**, once formed, is sufficiently excited to isomerize to **2**; the barrier for this process (63.5 kcal mol^{-1}) is lower than the exothermicity of its formation. Furthermore, isomer **2** is trapped in a relatively deep potential well considering that its dissociation into HF and $FBNH_2^+$ requires 20.4 kcal mol^{-1}.

The energy-resolved CAD spectra of the $[BF_2,NH_3]^+$ ions shows that the loss of HF requires an energy slightly lower than that necessary to lose the NH_3 molecule.

It is reasonable to assume that the $[BF_2,NH_3]^+$ ionic population certainly contains the $F_2BNH_3^+$ ions characterized by isomer **1** connectivity, whereas the possible formation of isomer **2** can be excluded. In fact, isomer **1** is the only species responsible for the fragmentation into BF_2^+ and NH_3 (92.7 kcal mol^{-1}) and may lose the HF molecule through the isomerization into **2** and its subsequent dissociation, a process requiring 67.3 kcal mol^{-1}. On the basis of these energetic considerations, the possible existence of isomer **2** can be excluded. The loss of HF, the only fragmentation characteristic of this species, requires an energy (20.4 kcal mol^{-1}) that is undoubtedly too low with respect to the threshold values observed in the CAD spectra.

Concerning the $[BF,NH_2]^+$ ion structure, it is reasonable to assume that this species, generated by the loss of the HF molecules from the $F_2B-NH_3^+$ ions, is characterized by the $FB-NH_2$ connectivity characteristic of isomer **3**.

The $[BF,NH_2]^+$ ion loses the NH radical in the triplet ground state at lower energies than the NH_2 and F moieties, although all these fragmentation are characterized by very high threshold energy values. The latter dissociations, requiring 164.7 and 168.1 kcal mol^{-1}, respectively, are peculiar of isomer **3** and indicate its formation. Furthermore, also the dissociation into ^3NH and FBH^+, characteristic of isomer **4**, is indicative of isomer **3** formation. In fact, this dissociation requires only 48.9 kcal mol^{-1} from **4**, an energy too low with respect to that measured in the CAD spectra. On the contrary, the appearance energy of the FBH^+ fragments through the isomerization of **3** into **4** and its subsequent dissociation, requires 136.3 kcal mol^{-1}, an energy compatible with the threshold values observed in the CAD spectra.

The existence of isomer **4** can be ruled out on the basis of energetic consideration since the barrier for its formation from **3** (113.1 kcal mol^{-1}) is considerably higher than the exothermicity of the process leading to **3** formation. Moreover, protomer **4** is characterized by an easy fragmentation into BNH^+ and HF, a process never observed in the CAD spectra.

The diamidoboron cation, $[B(NH_{2)2}]^+$, is characterized by the NH_2-B-NH_2 structure. Also, this species is particularly stable considering the high collision energy value necessary to break the boron−nitrogen bond.

The $F_2B-NH_3^+$ ions represent the protonated form of aminodifluoroborane, the primary volatile product obtained in the pyrolysis of the F_3B-NH_3 complex.[23] Consequently, this ionic species behaves in FT-ICR conditions as a Brønsted acid. The PA of BF_2-NH_2 can be roughly positioned between H_2O (PA = 165.0 kcal mol^{-1}) and HN_3 (PA = 180.7 kcal mol^{-1}).

The electron-deficient boron atom of the $FBNH_2^+$ species is able to add Lewis bases such as H_2O, NH_3, and HN_3. The loss of HF or N_2 from the initially formed complexes leads to interesting new ionic species such as $[NH_2BOH]^+$ and $[NH_2,BF,NH]^+$. The formation of the diamidoboron cation from the reaction with NH_3 may represent the first step of the ionic processes eventually leading to the generation of molecules characterized by a $B-NH_2$ chain. Unfortunately, we cannot isolate the $NH_2-B-NH_2^+$ ions and let them react with neutral BF_3 in order to verify the possible formation of longer species containing the BNH_2 unity.

The $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) ions and the diamidoboron cation, $NH_2-B-NH_2^+$, are characterized by strong B−N bonds and hence could be considered ideal candidates for boron nitride deposition with techniques involving high-energy ion beams.

Conclusions

The addition of BF_2^+ to ammonia leads to the first observation of $[BF_nNH_{n+1}]^+$ ($n = 1, 2$) ions. The joint application of mass-spectrometric and ab initio theoretical methods allows the new ionic species to be identified and structurally characterized as $F_2B-NH_3^+$ and $FB-NH_2^+$. The $F_2B-NH_3^+$ ion represents the protonated form of aminodifluoroborane, BF_2NH_2, and, consequently, behaves as a Brønsted acid under FT-ICR conditions undergoing H^+ transfer to selected bases having a PA of at least 180.7 kcal mol^{-1}.

The $FBNH_2^+$ ion forms donor−acceptor complex with hard Lewis bases such as water, ammonia, and hydrazoic acid.

All these species represent promising precursors for boron nitride deposition through conventional methods involving high-energy ion beams. Attempts to deposit boron nitride films using low-energy ion beams containing these species are under way in our laboratory.

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References and Notes

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