



Article **F₂BMF (M = B and Al) Molecules: A Matrix Infrared Spectra and Theoretical Calculations Investigation**

Juanjuan Cheng¹, Liyan Cai¹, Zhen Pu², Bing Xu^{1,*} and Xuefeng Wang^{1,*}

- ¹ Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China
- ² China Academy of Engineering and Physics, Mianyang 621900, China
- * Correspondence: xbrare@tongji.edu.cn (B.X.); xfwang@tongji.edu.cn (X.W.)

Abstract: Reactions of laser-ablated B and Al atoms with BF₃ have been explored in the 4 K excess neon through the matrix isolation infrared spectrum, isotopic substitutions and quantum chemical calculations. The inserted complexes F_2BMF (M = B, Al) were identified by anti-symmetric and symmetric stretching modes of F-B-F, and the F-¹¹B-F stretch modes are at 1336.9 and 1202.4 cm⁻¹ for $F_2^{11}B^{11}BF$ and at 1281.5 and 1180.8 cm⁻¹ for $F_2^{11}BAIF$. The CASSCF analysis, EDA-NOCV calculation and the theory of atoms-in-molecules (AIM) are applied to investigate the bonding characters of F_2BBF and F_2BAIF molecules. The bonding difference between boron and aluminum complexes reveals interesting chemistries, and the FB species stabilization by a main group atom was first observed in this article.

Keywords: inserted complexes F₂BMF; BF₃; infrared spectrum; quantum chemical calculations

1. Introduction

B₂ species, comprising electron-precise B-B bonds, have witnessed swift developments in the past twenty years, in which B_2X_n (X = F, Cl, Br, n = 2,4) molecules are important precursors for synthesizing boron-containing compounds, which garnered much attention from scientists [1]. As for B_2F_4 , Trefonas and Lipscomb showed that B_2F_4 has a planar structure in the solid phase by X-ray diffraction [2], while several earlier Raman and infrared spectroscopic studies suggested a staggered structure [3–5]. In 1977, Danielson, Patton, and Hedberg confirmed that the gaseous B_2F_4 molecule has a D_{2h} symmetry by electron diffraction [6]. Fan and Li also found that the ground state of B_2F_4 has an eclipsed conformation (in D_{2h} symmetry) [6]. Later, Danielson, Patton, and Hedberg demonstrated that the experimental difficulties in determining the structure of B_2F_4 were probably due to its very low internal rotation barrier around the B-B bond (0.42 kcal·mol) [7]. For F_2B_2 , the linear singlet structure FBBF ($D_{\infty h}$, ${}^{3}\Sigma^{-}$) is a second-order stationary point at MBPT(2), and it could convert into a bent structure $(C_{2h}, {}^{1}A_{g})$, which is 5.0 kcal/mol higher in energy than a linear structure at MBPT(2) [8]. The double-bond character for the bent structure is suggested by the NBO analysis (WBI-[BB] = 1.432 Å), involving two highest occupied ag and bu MO's, which can be visualized as a donor-acceptor complex formed by the delocalization of σ lone pairs into empty p_{π} orbitals lying in the molecular plane. The association of two ground-state BF molecules into the C_{2h} bent structure has a very low barrier (<1.0 kcal/mol) via a loose C_{2h} symmetric transition state ($R_{BB} = 2.434 \text{ Å}$) [8]. Recently, our assignment of the experimentally observed B-F stretching frequencies at 1327 cm⁻¹ to the trans-bent isomer FBBF is therefore very tentative due to similarity in the calculated anti-symmetric B-F stretching frequencies of the linear and bent isomers [9].

Although B_2F_4 and B_2F_2 have already been known well, there seems to be no relevant report on the B_2F_3 molecule. As we know, B_2F_3 should possesse FB₂ and FB fragments, having significant differences from B_2F_4 and B_2F_2 molecules, but its structure and properties have not yet been understood. Boron is the main group element in the periodic



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). table, and bonding between boron and main group elements has also been an attractive subject [10–14]. For example, by laser vaporization of a mixed B/Bi target, the Bi \equiv B and Bi = B multiple bonds in BiB₂O₂⁻ and Bi₂B⁻ are observed and are characterized by photoelectron spectroscopy and ab initio calculations [15]. Several years ago, we reported some boryl complexes F₂BMF (M = C, Si, Ge, Sn, Pb) [14], and DFT and CCSD(T) calculations demonstrate that triplet F₂BCF is the most stable isomer with two singly occupied molecular orbitals, while singlet F₂BMF (M = Si, Ge, Sn and Pb) molecules possess a near right angle B-M-F moiety with lone pair electrons on the M atom. In this paper, the laser-ablated B and Al were demonstrated to react with BF₃ to produce the fluoroboryl complexes F₂BBF and F₂BAIF, which have been identified by boron isotopic substitution and theoretical frequency calculations. The bonding formation for B-B as well as B-Al in fluoroboryl complexes of F₂BMF was investigated by EDA-NOCV and CASSCF calculations. The active molecular orbital and NBO analysis, and the bonding difference, were analyzed in detail.

2. Results and Discussion

The assignment of absorptions was based on the behavior of the products' absorptions upon stepwise annealing and photolysis behavior and will be discussed below. The typical infrared spectra in the selected regions and the absorption bands are shown in Figures 1–3 and Table 1, respectively. In addition, the calculated frequencies based on DFT are listed in the same tables for comparison.



Figure 1. Infrared spectra of the laser-ablated B atoms' reactions with BF₃ in excess solid neon. (a) co-deposition of ¹¹B + 1.0% ¹¹BF₃ for 60 min; (b) after annealing to 8 K; (c) after λ > 300 nm irradiation for 6 min; (d) after annealing to 12 K; (e) co-deposition of ¹⁰B + 0.5% ¹⁰BF₃ for 60 min; (f) after annealing to 8 K; (g) after λ > 300 nm irradiation for 6 min; (h) after annealing to 12 K.



Figure 2. Infrared spectra of the laser-ablated B react with BF₃ in excess solid neon. (**a**) co-deposition of ${}^{10}\text{B} + 1.0\%$ ${}^{11}\text{BF}_3$ for 60 min; (**b**) after annealing to 8 K; (**c**) after $\lambda > 300$ nm irradiation for 6 min; (**d**) $\lambda > 220$ nm irradiation for 6 min; (**e**) co-deposition of ${}^{11}\text{B} + 0.5\%$ ${}^{10}\text{BF}_3$ for 60 min; (**f**) after annealing to 8 K; (**g**) after $\lambda > 300$ nm irradiation for 6 min; (**h**) $\lambda > 220$ nm for irradiation for 6 min.



Figure 3. Infrared spectra of the laser-ablated Al atoms reactions with BF₃ in excess solid neon. (a) co-deposition of Al + 0.5% ¹¹BF₃ for 60 min; (b) after annealing to 8 K; (c) after λ = 450 nm irradiation for 6 min; (d) after annealing to 12 K; (e) co-deposition of Al + 0.5% ¹⁰BF₃ for 60 min; (f) after annealing to 8 K; (g) after λ = 450 nm irradiation for 6 min; (h) after annealing to 12 K.

| Approximate Description | Obs(Ne) | Cal(int) ^a | Cal(int) ^b | Cal(int) ^c | Obs(Ne) | Cal(int) ^a | Cal(int) ^b | Cal(int) ^c |
|-----------------------------|---------|-----------------------|-----------------------|-----------------------|---------|-----------------------|-----------------------|-----------------------|
| BBFantisymstr | / | 1491.2(52) | 1461.7(50) | 1466.2 | / | 1501.4(41) | 1471.7(37) | 1477.8 |
| BF ₂ antisymstr | 1336.9 | 1332.3(294) | 1286.7(265) | 1376.3 | 1369.4 | 1378.8(317) | 1331.6(284) | 1425.1 |
| BF ₂ symstr | 1202.4 | 1188.9(465) | 1150.9(427) | 1213.6 | 1223.8 | 1221.3(505) | 1182.6(465) | 1245.4 |
| | | | $F_2{}^{11}B^{10}BF$ | | | | $F_2{}^{10}B^{10}BF$ | |
| BBFantisymstr | / | 1538.6(70) | 1508.0(63) | 1511.4 | / | 1546.82(56) | 1516.6(49) | 1520.8 |
| BF ₂ antisymstr | 1338.7 | 1332.3(294) | 1286.7(265) | 1376.3 | 1370.6 | 1378.90(324) | 1331.6(284) | 1425.1 |
| BF ₂ symstr | 1200.8 | 1192.3(462) | 1154.2(424) | 1217.9 | 1241.6 | 1226.32(505) | 1187.3(463) | 1251.9 |
| | | | F2 ¹¹ BAlF | | | | F2 ¹⁰ BAlF | |
| BF ₂ antisymmstr | 1281.5 | 1312.0(277) | 1270.9(257) | 1342.1 | 1324.6 | 1357.4(299) | 1314.9(275) | 1389.1 |
| BF ₂ symstr | 1180.8 | 1172.2(320) | 1133.9(309) | 1190.3 | 1217.1 | 1208.2(378) | 1168.8(336) | 1227.4 |
| AlFstr | 819.6 | 806.7(106) | 780.1(98) | 814.5 | 819.6 | 806.8(106) | 780.2(98) | 814.6 |

Table 1. Observed and calculated fundamental frequencies of F_2BBF and F_2AlBF isotopomers in the ground ²A state.

The vibrational frequencies (cm⁻¹) and intensities (km/mol, in parentheses) are calculated using: ^a B3LYP/def2-TZVPP; ^b BPW91/def2-TZVPP; ^c CCSD(T)/def2-TZVP(-f) functionals/basis set.

2.1. F₂BBF

In the reaction of laser-ablated ¹¹B with ¹¹BF₃ in excess neon, as shown in the Figure 1, the new product absorptions upon co-deposition appeared at 1336.9 and 1202.4 cm⁻¹. These two bands decreased slightly after annealing to 8 K and 12 K. These two bands shifted to 1370.6 and 1241.6 cm⁻¹ in the reaction of ¹⁰BF₃ with the ¹⁰B target, which showed the similar behavior to that of the counterparts produced with ¹¹B + ¹¹BF₃.

The 1336.9 cm⁻¹ appeared at the BF₂ stretching region and shifted to 1370.6 cm⁻¹ with ${}^{10}\text{BF}_3 + {}^{10}\text{B}$, giving the 1.0252 ${}^{10}\text{B}/{}^{11}\text{B}$ isotopic frequency ratio, which are in good agreement with the isotopic frequency ratio of 1.0280 in the B₂F₄ molecule [3]. The 1202.4 cm⁻¹ shifted to 1241.6 cm⁻¹, giving the ${}^{10}\text{B}/{}^{11}\text{B}$ isotopic frequency ratio of 1.0326 that was close to the calculated ratio of 1.0350 and fit in the previously reported values of the F-B-F vibration mode [16]. Unfortunately, the BBF stretching mode was covered by precursor bands in our experiments. These bands are appropriate for the F₂B-BF molecule based on the isotopic shifts and photochemical behavior.

In the reaction of ¹¹BF₃ with ¹⁰B target (Figure 2a–d), two new bands appeared at 1338.7 and 1200.8 cm⁻¹ in the BF₂ stretching region, which decreased slightly after annealing to 8 K and λ > 300 nm photolysis, and decreased obviously after λ > 220 nm irradiation. In addition, the other new group bands appeared at 1369.4 and 1223.8 cm⁻¹ after λ > 220 nm irradiation. In the reaction of ¹⁰BF₃ with ¹¹B (Figure 2e–h), 1369.4 and 1223.8 cm⁻¹ bands appeared on deposition, which decreased largely upon λ > 220 nm irradiation. Meanwhile, new group bands were located at 1338.7 and 1200.8 cm⁻¹ after λ > 220 nm photolysis. Obviously, we obtained the same two isomers in ¹⁰BF₃ + ¹¹B and ¹¹BF₃ + ¹⁰B experiments.

It is very interesting to observe that in the reaction of ¹¹BF₃ with ¹⁰B (Figure 2a–d), $F_2^{11}B^{10}BF$ was produced at first, but decreased with the emergence of $F_2^{10}B^{11}BF$ on >220 nm irradiation. Similarly, in Figure 2e–h, $F_2^{10}B^{11}BF$ was observed firstly and then $F_2^{11}B^{10}BF$ appeared accompanied with no obvious change of $F_2^{10}B^{11}BF$ on the >220 nm irradiation. Apparently, α -F transfer happened between the two species due to the photo irradiation.

This assignment is supported by our DFT frequency calculations (Table 1). The F_2BBF molecule is predicted to have C_s symmetry with ²A ground state (Figure 4). The antisymmetric and symmetric B-F stretching modes of the $F_2^{11}B(^{10}B)^{-11}BF$ molecule were predicted at 1332.3 (1378.8) and 1188.9 (1221.3) cm⁻¹ using the B3LYP functional, very close to our observed values of 1336.9 (1369.4) and 1202.4 (1223.8) cm⁻¹. Furthermore, the anti-symmetric and symmetric B-F stretching modes of the $F_2^{11}B(^{10}B)^{-10}BF$ molecule were predicted at 1332.3 (1378.9) and 1192.3 (1226.3) cm⁻¹, which are in good agreement with our observed values at 1338.7 (1370.6) and 1200.8 (1241.6) cm^{-1} . The results of BPW91 and CCSD(T) are consistent with that of B3LYP.



Figure 4. Structures of the product F_2BMF (M = B, Al) optimized using the CCSD(T)/def2-TZVP(-f) (**bold** and *italic*), CAS(9e, 11o)/def2-TZVP, BPW91/def2-TZVPP (*italic*) and B3LYP/def2-TZVPP (**bold**) functionals/basis set. The def2-TZVP(-f), def2-TZVP and def2-TZVPP basis are set for all atoms. Bond lengths are in Å and angles in degrees. The energies are in kcal/mol and relative to corresponding M + BF₃ calculated by CCSD(T)/def2-TZVPP.

2.2. F_2BAlF

As shown in Figure 3 and Table 1, the new product absorptions located at 1281.5, 1180.8 and 819.6 cm⁻¹ in the reaction of ¹¹BF₃ with laser-ablated Al atoms, increased on annealing to 8 K, but decreased sharply on the λ = 450 nm irradiation and increased again on annealing to 12 K. These bands shifted to 1324.6, 1217.1 and 819.6 cm⁻¹ in the reaction of ¹⁰BF₃ with Al atoms, which showed a similar response to kinds of photolysis and annealing.

The absorption bands at 1281.5 and 1180.8 cm⁻¹ shifted to 1324.6 and 1217.1 cm⁻¹, giving 1.0336 and 1.0307 of ${}^{10}B/{}^{11}B$ isotopic frequency ratio, which match very well with the F-B-F radical vibration mode [16]. The absorption bands at 819.6 cm⁻¹ showed no ${}^{10}B/{}^{11}B$ isotopic frequency ratio shift, indicating that only Al and F are involved in this mode. It is most likely that this absorption arises from terminal Al–F stretching vibrations. All these indicate that this group band is attributable to the F₂BAIF molecular.

The B3LYP calculations predict the F₂BAIF molecule to have C_S symmetry with ²A ground state. The calculated BF₂ anti-symmetric and symmetric mode using B3LYP is 1312.0 and 1172.2 cm⁻¹, being overestimated by about 2.3% and underestimated by about 0.7%, respectively. The calculated Al-F stretching vibration is overestimated by about 1.6%, which fits the observed values very well.

3. Reaction Product Comparison and Bonding Consideration

Two stable complexes, F₂BBF and F₂BAlF, were calculated by the B3LYP functional and parameters are illustrated in Figure 4. The reaction of laser-ablated B atoms with BF₃ to produce inserted complex F₂BBF is exothermic by 54.0 kcal/mol at CCSD(T) level. The subsequent α -F transfer reaction to give FBBF₂ requires an energy barrier of 31.7 kcal/mol. In our experiments of ¹¹BF₃ with ¹⁰B or ¹⁰BF₃ with ¹¹B, only one inserted species was observed first and then α -F transfer occurs upon 220 nm photolysis. In the reaction of BF₃ with Al atom, the F₂BAlF molecule is produced with an exothermic 15.5 kcal/mol⁻¹ reaction at the CCSD(T) level. However, the FB-AlF₂ produced by a-F transfer from F₂B-AlF is endothermic by 6.8 kcal/mol⁻¹, which could not be observed in our experiments (Figure 5).



Figure 5. Potential energy surface of group 13 atoms (B and Al) and BF₃ reaction products calculated at CCSD (T)/def2-TZVPP level. Energies were given in kcal/mol.

The bond angle of B-B-F for the F₂B-BF molecule is 142°, which is quite different from the 116° of B-Al-F angle for F_2 B-AlF (Figure 4). As shown in Figure 6a, for the F_2 BBF molecule, the B = B bond is composed of one σ bond with an occupation of 1.94 e and one $(p-p) \pi$ bond with an occupation of 1.00 e in the plane, which leads to a larger B-B-F bond angle. The effective bond order (EBO) of B-B bond is 1.32 calculated by natural bond orbital (NBO) population analysis. The calculated 1.644 Å of B = B bond length is shorter than that of B-B single bond between 1.819 and 1.859 Å, but longer than 1.561 and 1.590 Å of the B = B double bond length in R(H)B = B(H)R (R = :C{N(2,6- Pri₂C₆H₃)CH}₂) [17], and in OC(H)B = B(H)CO[18], respectively, affirming that B-B bond order in F₂B-BF is between one and two. Notice that for the F_2BAIF molecule, the effective bond order (EBO) of B-Al is 0.96 with an occupation of 1.93 e in the σ character (Figure 6b). The Al atom possesses a single electron (mostly from the *s* orbital) which does not participate in bonding. Although B and Al atom are in the same group, their bonding situation is very different. As shown in Table S1, for the F_2BBF molecule, both boron atoms have a good hybridization with the s and *p* orbital, while little hybridization occurs between the s and p orbital for the B-Al σ bond in the F₂BAlF molecule.



Figure 6. (a) The active molecular orbitals of F₂BBF at CASSCF (3e, 8o)/def2-TZVP level. The isosurface value is 0.04 a.u. MO occupation numbers are given with each orbital; (b) The active molecular orbitals of F₂BAIF at CASSCF (3e, 8o)/def2-TZVP level. The isosurface value is 0.04 a.u. MO occupation numbers are given with each orbital; (c) Plot of the deformation densities $\Delta\rho$ of the F₂B \rightarrow BF σ donation and BF \rightarrow BF₂ π back-donation in F₂BBF with the associated interaction energy Δ Eorb and charge eigenvalues $|\nu_n|$ (in e). The charge flow is from red \rightarrow blue; (d) Plot of the deformation in F₂BAIF with the associated interaction energy Δ Eorb and charge eigenvalues $|\nu_n|$ (in e). The charge flow is from red \rightarrow blue; from red \rightarrow blue.

The energy decomposition analysis (EDA) can be used in quantitative interpretation of chemical bonds' formation in terms of three major components (Table 2) [19]. For the F_2BBF molecule, the EDA shows that the total interaction energy of -148.3 kcal/mol between the F_2B and BF fragments consists of an attractive electrostatic energy of -53.0 kcal/mol, an orbital interaction energy of -193.9 kcal/mol and a large Pauli repulsion of 97.5 kcal/mol. This interaction energy is bigger than that of the H-H single bond (-112.9 kcal/mol), but smaller than the N-N triple bond's (-232.2 kcal/mol) [19]. Surprisingly, this interaction between B and B is bigger than that of the triple bond between B and heavier transition metal atom that we observed previously [20]. It is possible to breakdown the orbital term ΔE_{orb} into pairwise orbital contributions of the interacting fragments by EDA–Natural Orbitals for the Chemical Valence (NOCV) method [21–23]. Figure 6c clearly depicted the natural orbitals for the chemical valence of F_2BBF . The σ bond between B and B is mainly caused by the outflow of electrons (most 2s electron of B) from FB to B of BF₂ and then the $(p-p) \pi$ bond is formed by the outflow of one 2p electrons of B of BF₂ to 2p vacant orbital of B of BF. The decomposition of the orbital interaction shows that 42.7% (-82.8 kcal/mol) come from the σ bond, while 53.6% (-104.0 kcal/mol) come from the π bonds, respectively.

| Orbitals | F_2BBF (² A) | Orbitals | F_2BA1F (² A) |
|----------------------------------|----------------------------|----------------------------------|-----------------------------|
| $\Delta E_{\rm int}$ | -148.3 | $\Delta E_{\rm int}$ | -28.84 |
| ΔE_{Pauli} | 97.5 | $\Delta E_{\mathrm{Pauli}}$ | 111.5 |
| $\Delta E_{ m elstat}$ | -53.0 (21.5%) | $\Delta E_{\mathrm{elstat}}$ | -60.4 (42.8%) |
| $\Delta E_{\rm orb}$ | -193.9 (78.5%) | $\Delta E_{\rm orb}$ | -80.7 (57.2%) |
| ΔE_{σ} | -82.82 (42.7%) | ΔE_{σ} | -29.9 (37.1%) |
| ΔE_{π} | -104.0 (53.6%) | ΔE_{σ} | -42.2 (52.3%) |
| $\Delta E_{\rm orb}({\rm rest})$ | -7.1 (3.7%) | $\Delta E_{\rm orb}({\rm rest})$ | -8.6 (15.6%) |
| $\Delta E_{\rm dist}$ | 1.1 | $\Delta E_{\rm dist}$ | 0.76 |

Table 2. The results of EDA-NOCV theory for F_2BMF at B3LYP/TZ2P.

Energy values are given in kcal/mol.

For the F₂BAlF molecular, only one σ bond existed between B and Al and both B and Al atom contribute to this σ bond together (Figure 6d). From Figure 6b, we can observe that the occupation of the σ bond is 1.93 e. Moreover, the Al atom possesses a single electron (most from the s orbital) which did not participate in bonding. Although B and Al atoms are in the same group, their bonding situation is very different. In Table S1, for the F₂BBF molecule, both two boron atoms have good hybridization with the s and p orbital. While for the B-Al σ bond, the bonding electron is either from the *s* orbital or from the *p* orbital of the Al atom in a different phase and little hybridization happening between the *s* and *p* orbital. Thus, the 3s electrons of aluminum barely participates in bonding with other atoms and no π bond formed in the F₂BAlF molecule.

Although the FBAlF₂ molecule was not observed in the experiment by the α -F transfer, a similar bonding composition could be demonstrated to that of FBBF₂ (Figure S1). The B-Al is also caused by the outflow of electrons (most 2*s* electron of B) from FB to Al, and then the (p-p) π bond is formed by the inflow of one 3*p* electrons of Al to the 2*p* vacant orbital of B. The total interaction energy of -122.0 kcal/mol between BF and AlF₂ is very strong, and 29.3% (-39.5 kcal/mol) come from the σ bond and 68.3% (-91.9 kcal/mol) from π bond; thus, compounds with σ -donor and π -acceptor bonding modes formed [20].

For further analyzing the bond character, the atoms in the molecule theory (AIM) analysis were performed (Figure S2). The negative value of local energy density H(r) = -0.12656 and -0.02651 for B-B and B-Al was obtained, respectively. The bond critical point between the B and B atom locates in the negative value of the Laplacian value ($\nabla^2 \rho_{cp} = -0.426$); however, this value is slightly positive ($\nabla^2 \rho_{cp} = 0.058$) and close to zero between the B and Al atom. Figure S3 displayed the color-filled maps of the localized orbital locator (LOL) on the F₂BM (B, Al) plane. It demonstrated that there are high electron localization regions between boron and metal (B and Al), which indicates the covalent bond character. From B to Al, the BF₂ antisymmetric and symmetric stretch mode can red-shift from 1336.9 and 1202.4 cm⁻¹ to 1281.5 and 1180.8 cm⁻¹.

4. Experimental and Computational Methods

Laser-ablated B and Al atoms react with ${}^{11}\text{BF}_3$ and ${}^{10}\text{BF}_3$ in excess neon during condensation at 4 K using a closed-cycle helium refrigerator (Sumitomo Heavy Industries Model SRDK-408D2, Japan). A Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto the rotating B, or Al target, and typically 20–30 mJ/pulse was used. The laser-ablated enriched ${}^{10}\text{B}$ (Eagle Pitcher, America, 93.8% ${}^{10}\text{B}$, 6.2% ${}^{11}\text{B}$), enriched ${}^{11}\text{B}$ (Eagle Pitcher, 97.5% ${}^{11}\text{B}$, 2.5% ${}^{10}\text{B}$), and Al (Alfa Aesar, America, 99.999%) atoms were reacted with ${}^{11}\text{BF}_3$ and ${}^{10}\text{BF}_3$ purchased from Jinglin (Shanghai, China) Chemical Industry Limited Liability Company (Shanghai, China, chemical purity, \geq 99.99%) in excess neon spread uniformly onto the CsI window. Infrared spectra were recorded at a resolution of 0.5 cm⁻¹ between 4000 and 400 cm⁻¹ using a HgCdTe range B detector.

Selected samples were irradiated by a mercury lamp (175 W, without globe) with the aid of glass filters to permit the allowed wavelengths to pass.

All structures were optimized at the BPW91/def2-TZVPP and B3LYP/def2-TZVPP [24,25] basis set via the Gaussian 09 program [26] and CAS(9e, 11o)/def2-TZVP [27,28] and CCSD(T)/def2-TZVP(-f) [29–31] basis set via the ORCA 4.0.1 program [32,33]. The single point energy calculations were performed with the correlated molecular orbital theory coupled cluster CCSD(T) [29–31] theory. Transition states were optimized with the Rational Function Optimization (RFO) method and were verified to link the desired reactant and product through the intrinsic reaction coordinate (IRC) calculations. Atoms in molecules' (AIM) [34] analysis was performed to elicit detailed information on the bonding characters with the Multiwfn code [35]. The orbital composition and effective bond order and Wiberg bond order were calculated by a natural bond orbital (NBO) population analysis [26,36]. In addition, ab initio calculations based on the high-level multi-configurational wavefunction method were also performed to obtain the accurate electronic structure information of BF₂-MF compounds by the ORCA 4.0.1 program [32,33]. CASSCF [27] calculations including three active electrons in eight active orbitals [CAS(3e, 8o)], and NEVPT2 [37-39] calculations including three active electrons in four active orbitals [CAS(3e, 4o)] were performed with the def2-TZVP [28] basis set for all atoms. The effect of the dynamic correlation was taken into account by NEVPT2 [37–39] on top of the wavefunctions at CASSCF level to obtain more accurate energies. The energy decomposition analysis with the natural orbitals of the chemical valence (EDA-NOCV) method [21–23] were carried out with the ADF 2017 program [40] package to study the chemical bonding between the B and Al atoms with the B atom.

5. Conclusions

The reaction of laser-ablated B and Al atoms with BF₃ has been studied by the matrix isolation infrared spectrum and theoretical calculations. The structure and properties of the B₂F₃ molecule, which can be drawn as F₂B-BF, have been investigated. The F-B-F stretching mode was located at 1336.9 and 1202.4 cm⁻¹. For comparison, the F₂BAlF molecule was also investigated and the F-B-F stretching mode was at 1281.5 and 1180.8 cm⁻¹. The CASSCF analysis, EDA-NOCV calculation, the theory of atoms-in-molecules (AIM) and localized orbital locator (LOL) are applied to investigate the bonding characters of the B-B and B-Al bond in F₂BBF and F₂BAlF molecules. The B-B bond in F₂BBF favors the one and half bond order, in which two boron atoms have a good hybridization between *s* and *p* orbital. Meanhile, due to little hybridization between *s* and *p* orbital, 3s electrons of aluminum barely participate in bonding with other atoms, thus one bond order is formed for the B-Al bond.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/molecules28020554/s1, Figure S1: Plot of the deformation densities $\Delta \rho$ of the BF \rightarrow AlF₂ σ donation and AlF₂ \rightarrow BF π back-donation in FBAlF₂ with the associated interaction energy ΔE_{orb} and charge eigenvalues $|\nu_n|$ (in e).; Figure S2: Contour line diagrams of the Laplacian of the electronic density of F₂BMF (M = B, Al).; Figure S3: Color-filled maps of localized orbital locator of F₂BMF molecules (M = B, Al).; Table S1: Compositions of Natural Bond Orbitals from NBO Analysis of F₂BMF molecules (M = B, Al).; Table S2: Effective Bond Order Computed at B3LYP/def2-TZVPP level of F₂BMF molecules (M = B, Al).; Table S3: Calculated Fundamental Frequencies of F₂BBF and F₂AlBF isotopomers in the Ground ²A State.

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