# $\mathrm{F}_{2}$ BMF ( $\mathrm{M}=\mathrm{B}$ and A1) Molecules: A Matrix Infrared Spectra and Theoretical Calculations Investigation 

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#### Abstract

Reactions of laser-ablated B and Al atoms with $\mathrm{BF}_{3}$ have been explored in the 4 K excess neon through the matrix isolation infrared spectrum, isotopic substitutions and quantum chemical calculations. The inserted complexes $\mathrm{F}_{2} \mathrm{BMF}(\mathrm{M}=\mathrm{B}, \mathrm{Al})$ were identified by anti-symmetric and symmetric stretching modes of F-B-F, and the F- ${ }^{11}$ B-F stretch modes are at 1336.9 and $1202.4 \mathrm{~cm}^{-1}$ for $\mathrm{F}_{2}{ }^{11} \mathrm{~B}^{11} \mathrm{BF}$ and at 1281.5 and $1180.8 \mathrm{~cm}^{-1}$ for $\mathrm{F}_{2}{ }^{11} \mathrm{BAIF}$. The CASSCF analysis, EDA-NOCV calculation and the theory of atoms-in-molecules (AIM) are applied to investigate the bonding characters of $\mathrm{F}_{2} \mathrm{BBF}$ and $\mathrm{F}_{2} \mathrm{BAlF}$ 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 $\mathrm{F}_{2} \mathrm{BMF}^{2} \mathrm{BF}_{3}$; infrared spectrum; quantum chemical calculations

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## 1. Introduction

$B_{2}$ species, comprising electron-precise $B-B$ bonds, have witnessed swift developments in the past twenty years, in which $\mathrm{B}_{2} \mathrm{X}_{\mathrm{n}}(\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br}, n=2,4)$ molecules are important precursors for synthesizing boron-containing compounds, which garnered much attention from scientists [1]. As for $\mathrm{B}_{2} \mathrm{~F}_{4}$, Trefonas and Lipscomb showed that $\mathrm{B}_{2} \mathrm{~F}_{4}$ 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 $B_{2} \mathrm{~F}_{4}$ molecule has a $\mathrm{D}_{2 \mathrm{~h}}$ symmetry by electron diffraction [6]. Fan and Li also found that the ground state of $\mathrm{B}_{2} \mathrm{~F}_{4}$ has an eclipsed conformation (in $\mathrm{D}_{2 h}$ symmetry) [6]. Later, Danielson, Patton, and Hedberg demonstrated that the experimental difficulties in determining the structure of $B_{2} F_{4}$ were probably due to its very low internal rotation barrier around the $\mathrm{B}-\mathrm{B}$ bond ( $0.42 \mathrm{kcal} \cdot \mathrm{mol}$ ) [7]. For $\mathrm{F}_{2} \mathrm{~B}_{2}$, the linear singlet structure $\operatorname{FBBF}\left(D_{\infty h},{ }^{3} \Sigma^{-}\right)$is a second-order stationary point at MBPT(2), and it could convert into a bent structure $\left(C_{2 h},{ }^{1} \mathrm{~A}_{\mathrm{g}}\right)$, which is $5.0 \mathrm{kcal} / \mathrm{mol}$ higher in energy than a linear structure at $\operatorname{MBPT}(2)$ [8]. The double-bond character for the bent structure is suggested by the NBO analysis (WBI-[BB] = $1.432 \AA$ ), involving two highest occupied $\mathrm{a}_{\mathrm{g}}$ and $\mathrm{b}_{\mathrm{u}}$ MO's, which can be visualized as a donor-acceptor complex formed by the delocalization of $\sigma$ lone pairs into empty $\mathrm{p}_{\pi}$ orbitals lying in the molecular plane. The association of two ground-state BF molecules into the $C_{2 h}$ bent structure has a very low barrier ( $<1.0 \mathrm{kcal} / \mathrm{mol}$ ) via a loose $C_{2 h}$ symmetric transition state $\left(\mathrm{R}_{\mathrm{BB}}=2.434 \AA\right)$ [8]. Recently, our assignment of the experimentally observed B-F stretching frequencies at $1327 \mathrm{~cm}^{-1}$ 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 $\mathrm{B}_{2} \mathrm{~F}_{4}$ and $\mathrm{B}_{2} \mathrm{~F}_{2}$ have already been known well, there seems to be no relevant report on the $B_{2} F_{3}$ molecule. As we know, $B_{2} F_{3}$ should possesse $F B_{2}$ and $F B$ fragments, having significant differences from $\mathrm{B}_{2} \mathrm{~F}_{4}$ and $\mathrm{B}_{2} \mathrm{~F}_{2}$ molecules, but its structure and properties have not yet been understood. Boron is the main group element in the periodic
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 $\mathrm{B} / \mathrm{Bi}$ target, the $\mathrm{Bi} \equiv \mathrm{B}$ and $\mathrm{Bi}=\mathrm{B}$ multiple bonds in $\mathrm{BiB}_{2} \mathrm{O}_{2}^{-}$and $\mathrm{Bi}_{2} \mathrm{~B}^{-}$are observed and are characterized by photoelectron spectroscopy and ab initio calculations [15]. Several years ago, we reported some boryl complexes $\mathrm{F}_{2} \mathrm{BMF}(\mathrm{M}=\mathrm{C}, \mathrm{Si}, \mathrm{Ge}, \mathrm{Sn}, \mathrm{Pb})[14]$, and DFT and $\mathrm{CCSD}(\mathrm{T})$ calculations demonstrate that triplet $\mathrm{F}_{2} \mathrm{BCF}$ is the most stable isomer with two singly occupied molecular orbitals, while singlet $\mathrm{F}_{2} \mathrm{BMF}(\mathrm{M}=\mathrm{Si}, \mathrm{Ge}, \mathrm{Sn}$ and Pb$)$ molecules possess a near right angle $\mathrm{B}-\mathrm{M}-\mathrm{F}$ moiety with lone pair electrons on the M atom. In this paper, the laser-ablated B and Al were demonstrated to react with $\mathrm{BF}_{3}$ to produce the fluoroboryl complexes $\mathrm{F}_{2} \mathrm{BBF}$ and $\mathrm{F}_{2} \mathrm{BAlF}$, which have been identified by boron isotopic substitution and theoretical frequency calculations. The bonding formation for $\mathrm{B}-\mathrm{B}$ as well as $\mathrm{B}-\mathrm{Al}$ in fluoroboryl complexes of $\mathrm{F}_{2}$ BMF 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 $\mathrm{BF}_{3}$ in excess solid neon. (a) co-deposition of ${ }^{11} \mathrm{~B}+1.0 \%{ }^{11} \mathrm{BF}_{3}$ for 60 min ; (b) after annealing to 8 K ; (c) after $\lambda>300 \mathrm{~nm}$ irradiation for 6 min ; (d) after annealing to 12 K ; (e) co-deposition of ${ }^{10} \mathrm{~B}+0.5 \%{ }^{10} \mathrm{BF}_{3}$ for 60 min ; (f) after annealing to 8 K ; (g) after $\lambda>300 \mathrm{~nm}$ irradiation for 6 min ; (h) after annealing to 12 K .


Figure 2. Infrared spectra of the laser-ablated $B$ react with $\mathrm{BF}_{3}$ in excess solid neon. (a) co-deposition of ${ }^{10} \mathrm{~B}+1.0 \%{ }^{11} \mathrm{BF}_{3}$ for 60 min ; (b) after annealing to 8 K ; (c) after $\lambda>300 \mathrm{~nm}$ irradiation for 6 min ; (d) $\lambda>220 \mathrm{~nm}$ irradiation for 6 min ; (e) co-deposition of ${ }^{11} \mathrm{~B}+0.5 \%{ }^{10} \mathrm{BF}_{3}$ for 60 min ; (f) after annealing to 8 K ; (g) after $\lambda>300 \mathrm{~nm}$ irradiation for $6 \mathrm{~min} ;(\mathbf{h}) \lambda>220 \mathrm{~nm}$ for irradiation for 6 min .


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

Table 1. Observed and calculated fundamental frequencies of $\mathrm{F}_{2} \mathrm{BBF}$ and $\mathrm{F}_{2} \mathrm{AlBF}$ isotopomers in the ground ${ }^{2} \mathrm{~A}$ state.

| Approximate Description | Obs(Ne) | Cal(int) ${ }^{\text {a }}$ | Cal(int) ${ }^{\text {b }}$ | Cal(int) ${ }^{\text {c }}$ | Obs(Ne) | Cal(int) ${ }^{\text {a }}$ | Cal(int) ${ }^{\text {b }}$ | Cal(int) ${ }^{\text {c }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| BBFantisymstr | 1 | 1491.2(52) | 1461.7(50) | 1466.2 | / | 1501.4(41) | 1471.7(37) | 1477.8 |
| $\mathrm{BF}_{2}$ antisymstr | 1336.9 | 1332.3(294) | 1286.7(265) | 1376.3 | 1369.4 | 1378.8(317) | 1331.6(284) | 1425.1 |
| $\mathrm{BF}_{2}$ symstr | 1202.4 | 1188.9(465) | 1150.9(427) | 1213.6 | 1223.8 | 1221.3(505) | 1182.6(465) | 1245.4 |
|  |  |  | $\mathrm{F}_{2}{ }^{11} \mathrm{~B}^{10} \mathrm{BF}$ |  |  |  | $\mathrm{F}_{2}{ }^{10} \mathrm{~B}^{10} \mathrm{BF}$ |  |
| BBFantisymstr | / | 1538.6(70) | 1508.0(63) | 1511.4 | / | 1546.82(56) | 1516.6(49) | 1520.8 |
| $\mathrm{BF}_{2}$ antisymstr | 1338.7 | 1332.3(294) | 1286.7(265) | 1376.3 | 1370.6 | 1378.90(324) | 1331.6(284) | 1425.1 |
| $\mathrm{BF}_{2}$ symstr | 1200.8 | 1192.3(462) | 1154.2(424) | 1217.9 | 1241.6 | 1226.32(505) | 1187.3(463) | 1251.9 |
|  |  |  | $\mathrm{F}_{2}{ }^{11} \mathrm{BAlF}$ |  |  |  | $\mathrm{F}_{2}{ }^{10} \mathrm{BAlF}$ |  |
| $\mathrm{BF}_{2}$ antisymmstr | 1281.5 | 1312.0(277) | 1270.9(257) | 1342.1 | 1324.6 | 1357.4(299) | 1314.9(275) | 1389.1 |
| $\mathrm{BF}_{2}$ 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 |

The vibrational frequencies $\left(\mathrm{cm}^{-1}\right)$ and intensities ( $\mathrm{km} / \mathrm{mol}$, in parentheses) are calculated using: ${ }^{\text {a }}$ B3LYP/def2TZVPP; ${ }^{\text {b }}$ BPW91/def2-TZVPP; ${ }^{\text {c }} \operatorname{CCSD}(\mathrm{T}) /$ def2-TZVP(-f) functionals/basis set.

## 2.1. $F_{2} B B F$

In the reaction of laser-ablated ${ }^{11} \mathrm{~B}$ with ${ }^{11} \mathrm{BF}_{3}$ in excess neon, as shown in the Figure 1, the new product absorptions upon co-deposition appeared at 1336.9 and $1202.4 \mathrm{~cm}^{-1}$. These two bands decreased slightly after annealing to 8 K and 12 K . These two bands shifted to 1370.6 and $1241.6 \mathrm{~cm}^{-1}$ in the reaction of ${ }^{10} \mathrm{BF}_{3}$ with the ${ }^{10} \mathrm{~B}$ target, which showed the similar behavior to that of the counterparts produced with ${ }^{11} \mathrm{~B}+{ }^{11} \mathrm{BF}_{3}$.

The $1336.9 \mathrm{~cm}^{-1}$ appeared at the $\mathrm{BF}_{2}$ stretching region and shifted to $1370.6 \mathrm{~cm}^{-1}$ with ${ }^{10} \mathrm{BF}_{3}+{ }^{10} \mathrm{~B}$, giving the $1.0252{ }^{10} \mathrm{~B} /{ }^{11} \mathrm{~B}$ isotopic frequency ratio, which are in good agreement with the isotopic frequency ratio of 1.0280 in the $\mathrm{B}_{2} \mathrm{~F}_{4}$ molecule [3]. The $1202.4 \mathrm{~cm}^{-1}$ shifted to $1241.6 \mathrm{~cm}^{-1}$, giving the ${ }^{10} \mathrm{~B} /{ }^{11} \mathrm{~B}$ 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 $\mathrm{F}_{2} \mathrm{~B}-\mathrm{BF}$ molecule based on the isotopic shifts and photochemical behavior.

In the reaction of ${ }^{11} \mathrm{BF}_{3}$ with ${ }^{10} \mathrm{~B}$ target (Figure 2a-d), two new bands appeared at 1338.7 and $1200.8 \mathrm{~cm}^{-1}$ in the $\mathrm{BF}_{2}$ stretching region, which decreased slightly after annealing to 8 K and $\lambda>300 \mathrm{~nm}$ photolysis, and decreased obviously after $\lambda>220 \mathrm{~nm}$ irradiation. In addition, the other new group bands appeared at 1369.4 and $1223.8 \mathrm{~cm}^{-1}$ after $\lambda>220 \mathrm{~nm}$ irradiation. In the reaction of ${ }^{10} \mathrm{BF}_{3}$ with ${ }^{11} \mathrm{~B}$ (Figure 2e-h), 1369.4 and $1223.8 \mathrm{~cm}^{-1}$ bands appeared on deposition, which decreased largely upon $\lambda>220 \mathrm{~nm}$ irradiation. Meanwhile, new group bands were located at 1338.7 and $1200.8 \mathrm{~cm}^{-1}$ after $\lambda>220 \mathrm{~nm}$ photolysis. Obviously, we obtained the same two isomers in ${ }^{10} \mathrm{BF}_{3}+{ }^{11} \mathrm{~B}$ and ${ }^{11} \mathrm{BF}_{3}+{ }^{10} \mathrm{~B}$ experiments.

It is very interesting to observe that in the reaction of ${ }^{11} \mathrm{BF}_{3}$ with ${ }^{10} \mathrm{~B}$ (Figure 2a-d), $\mathrm{F}_{2}{ }^{11} \mathrm{~B}^{10} \mathrm{BF}$ was produced at first, but decreased with the emergence of $\mathrm{F}_{2}{ }^{10} \mathrm{~B}^{11} \mathrm{BF}$ on $>220 \mathrm{~nm}$ irradiation. Similarly, in Figure $2 \mathrm{e}-\mathrm{h}, \mathrm{F}_{2}{ }^{10} \mathrm{~B}^{11} \mathrm{BF}$ was observed firstly and then $\mathrm{F}_{2}{ }^{11} \mathrm{~B}^{10} \mathrm{BF}$ appeared accompanied with no obvious change of $\mathrm{F}_{2}{ }^{10} \mathrm{~B}^{11} \mathrm{BF}$ on the $>220 \mathrm{~nm}$ irradiation. Apparently, $\alpha$ - F transfer happened between the two species due to the photo irradiation.

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


Figure 4. Structures of the product $\mathrm{F}_{2} \mathrm{BMF}(\mathrm{M}=\mathrm{B}, \mathrm{Al})$ optimized using the $\operatorname{CCSD}(\mathrm{T}) /$ def2-TZVP $(-\mathrm{f})$ (bold and italic), CAS(9e, 110)/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 $\AA$ and angles in degrees. The energies are in $\mathrm{kcal} / \mathrm{mol}$ and relative to corresponding $\mathrm{M}+\mathrm{BF}_{3}$ calculated by $\operatorname{CCSD}(\mathrm{T}) /$ def2-TZVPP.

## 2.2. $F_{2}$ BAlF

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

The absorption bands at 1281.5 and $1180.8 \mathrm{~cm}^{-1}$ shifted to 1324.6 and $1217.1 \mathrm{~cm}^{-1}$, giving 1.0336 and 1.0307 of ${ }^{10} \mathrm{~B} /{ }^{11} \mathrm{~B}$ isotopic frequency ratio, which match very well with the F-B-F radical vibration mode [16]. The absorption bands at $819.6 \mathrm{~cm}^{-1}$ showed no ${ }^{10} \mathrm{~B} /{ }^{11} \mathrm{~B}$ 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 $\mathrm{Al}-\mathrm{F}$ stretching vibrations. All these indicate that this group band is attributable to the $\mathrm{F}_{2} \mathrm{BAlF}$ molecular.

The B3LYP calculations predict the $\mathrm{F}_{2} \mathrm{BAlF}$ molecule to have $C_{S}$ symmetry with ${ }^{2} \mathrm{~A}$ ground state. The calculated $\mathrm{BF}_{2}$ anti-symmetric and symmetric mode using B3LYP is 1312.0 and $1172.2 \mathrm{~cm}^{-1}$, 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, $\mathrm{F}_{2} \mathrm{BBF}$ and $\mathrm{F}_{2} \mathrm{BAIF}$, were calculated by the B3LYP functional and parameters are illustrated in Figure 4. The reaction of laser-ablated B atoms with $\mathrm{BF}_{3}$ to produce inserted complex $\mathrm{F}_{2} \mathrm{BBF}$ is exothermic by $54.0 \mathrm{kcal} / \mathrm{mol}$ at $\operatorname{CCSD}(\mathrm{T})$ level. The subsequent $\alpha$ - F transfer reaction to give $\mathrm{FBBF}_{2}$ requires an energy barrier of $31.7 \mathrm{kcal} / \mathrm{mol}$. In our experiments of ${ }^{11} \mathrm{BF}_{3}$ with ${ }^{10} \mathrm{~B}$ or ${ }^{10} \mathrm{BF}_{3}$ with ${ }^{11} \mathrm{~B}$, only one inserted species was observed first and then $\alpha$-F transfer occurs upon 220 nm photolysis. In the reaction of $\mathrm{BF}_{3}$ with Al atom, the $\mathrm{F}_{2} \mathrm{BAlF}$ molecule is produced with an exothermic $15.5 \mathrm{kcal} / \mathrm{mol}^{-1}$ reaction at the $\operatorname{CCSD}(\mathrm{T})$ level. However, the $\mathrm{FB}-\mathrm{AlF}_{2}$ produced by a-F transfer from $\mathrm{F}_{2} \mathrm{~B}$ AlF is endothermic by $6.8 \mathrm{kcal} / \mathrm{mol}^{-1}$, which could not be observed in our experiments (Figure 5).


Figure 5. Potential energy surface of group 13 atoms ( B and Al ) and $\mathrm{BF}_{3}$ reaction products calculated at CCSD (T)/def2-TZVPP level. Energies were given in $\mathrm{kcal} / \mathrm{mol}$.

The bond angle of B-B-F for the $\mathrm{F}_{2} \mathrm{~B}-\mathrm{BF}$ molecule is $142^{\circ}$, which is quite different from the $116^{\circ}$ of $\mathrm{B}-\mathrm{Al}-\mathrm{F}$ angle for $\mathrm{F}_{2} \mathrm{~B}-\mathrm{AlF}$ (Figure 4). As shown in Figure 6a, for the $\mathrm{F}_{2} \mathrm{BBF}$ molecule, the $\mathrm{B}=\mathrm{B}$ bond is composed of one $\sigma$ 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 $1.644 \AA$ of $\mathrm{B}=\mathrm{B}$ bond length is shorter than that of $B-B$ single bond between 1.819 and $1.859 \AA$, but longer than 1.561 and $1.590 \AA$ of the $B=B$ double bond length in $R(H) B=B(H) R\left(R=: C\left\{N\left(2,6-\operatorname{Pri}_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right) C H\right\}_{2}\right)$ [17], and in $\mathrm{OC}(\mathrm{H}) \mathrm{B}=\mathrm{B}(\mathrm{H}) \mathrm{CO}[18]$, respectively, affirming that $\mathrm{B}-\mathrm{B}$ bond order in $\mathrm{F}_{2} \mathrm{~B}-\mathrm{BF}$ is between one and two. Notice that for the $\mathrm{F}_{2} \mathrm{BAlF}$ molecule, the effective bond order (EBO) of $\mathrm{B}-\mathrm{Al}$ is 0.96 with an occupation of 1.93 e in the $\sigma$ character (Figure 6 b ). 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 $\mathrm{F}_{2}$ BBF 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 $\sigma$ bond in the $\mathrm{F}_{2}$ BAlF molecule.
(a)


BB $\boldsymbol{\sigma}(\mathbf{1 . 9 5 0 )}$


BB $\boldsymbol{\sigma}^{*}(\mathbf{0 . 0 1 1 )}$
(c)

$\Delta E_{\text {orb }}(\sigma)=-82.82 ;$
$|v(\sigma)|=0.75$


BB $\boldsymbol{\pi}(\mathbf{0 . 9 9 3})$


BB $\pi^{*}(0.016)$

$\Delta E_{\text {orb }}(\pi)=-104.0 ;$
$|v(\pi)|=0.88$
(b)


BAl $\sigma^{*}(\mathbf{0 . 0 1 6 )}$


$$
\Delta E_{\text {orb }}(\sigma)=-29.90 ;
$$

$$
|v(\sigma)|=0.43
$$



Al LP * (0.006)

$\Delta E_{\text {orb }}(\sigma)=-42.20 ;$
$|\mathbf{v}(\sigma)|=0.58$

Figure 6. (a) The active molecular orbitals of $\mathrm{F}_{2} \mathrm{BBF}$ at CASSCF (3e, 8o)/def2-TZVP level. The isosurface value is $0.04 \mathrm{a} . \mathrm{u}$. MO occupation numbers are given with each orbital; (b) The active molecular orbitals of $\mathrm{F}_{2} \mathrm{BAlF}$ at CASSCF $(3 \mathrm{e}, 8 \mathrm{o}) /$ 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 $\mathrm{F}_{2} \mathrm{~B} \rightarrow \mathrm{BF} \sigma$ donation and $\mathrm{BF} \rightarrow \mathrm{BF}_{2} \pi$ back-donation in $\mathrm{F}_{2} \mathrm{BBF}$ with the associated interaction energy $\Delta$ Eorb and charge eigenvalues $\left|v_{\mathrm{n}}\right|$ (in e). The charge flow is from red $\rightarrow$ blue; (d) Plot of the deformation densities $\Delta \rho$ of the $\mathrm{F}_{2} \mathrm{~B} \rightarrow \mathrm{AlF} \sigma$ donation and $\mathrm{AlF} \rightarrow \mathrm{BF}_{2} \sigma$ back-donation in $\mathrm{F}_{2} \mathrm{BAlF}$ with the associated interaction energy $\Delta$ Eorb and charge eigenvalues $\left|\nu_{n}\right|$ (in e). The charge flow is 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 $\mathrm{F}_{2}$ BBF molecule, the EDA shows that the total interaction energy of $-148.3 \mathrm{kcal} / \mathrm{mol}$ between the $\mathrm{F}_{2} \mathrm{~B}$ and BF fragments consists of an attractive electrostatic energy of $-53.0 \mathrm{kcal} / \mathrm{mol}$, an orbital interaction energy of $-193.9 \mathrm{kcal} / \mathrm{mol}$ and a large Pauli repulsion of $97.5 \mathrm{kcal} / \mathrm{mol}$. This interaction energy is bigger than that of the $\mathrm{H}-\mathrm{H}$ single bond ( $-112.9 \mathrm{kcal} / \mathrm{mol}$ ), but smaller than the N-N triple bond's ( $-232.2 \mathrm{kcal} / \mathrm{mol}$ ) [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 $\Delta \mathrm{E}_{\text {orb }}$ into pairwise orbital contributions of the interacting fragments by EDA-Natural Orbitals for the Chemical Valence (NOCV) method [21-23]. Figure 6 c clearly depicted the natural orbitals for the chemical valence of $F_{2} B B F$. The $\sigma$ bond between $B$ and $B$ is mainly caused by the outflow of electrons (most $2 s$ electron of $B$ ) from $F B$ to $B$ of $\mathrm{BF}_{2}$ and then the (p-p) $\pi$ bond is formed by the outflow of one $2 p$ electrons of B of $\mathrm{BF}_{2}$ to $2 p$ vacant orbital of B of BF. The decomposition of the orbital interaction shows that $42.7 \%(-82.8 \mathrm{kcal} / \mathrm{mol})$ come from the $\sigma$ bond, while $53.6 \%(-104.0 \mathrm{kcal} / \mathrm{mol})$ come from the $\pi$ bonds, respectively.

Table 2. The results of EDA-NOCV theory for $\mathrm{F}_{2} \mathrm{BMF}$ at B3LYP/TZ2P.

| Orbitals | $\mathbf{F}_{\mathbf{2}} \mathbf{B B F} \mathbf{( ~}^{\mathbf{2} \mathbf{A})}$ | Orbitals | $\mathbf{F}_{\mathbf{2}} \mathbf{B A 1 F} \mathbf{( 2}^{\mathbf{2} \mathbf{A})}$ |
| :---: | :---: | :---: | :---: |
| $\Delta E_{\text {int }}$ | -148.3 | $\Delta E_{\text {int }}$ | -28.84 |
| $\Delta E_{\text {Pauli }}$ | 97.5 | $\Delta E_{\text {Pauli }}$ | 111.5 |
| $\Delta E_{\text {elstat }}$ | $-53.0(21.5 \%)$ | $\Delta E_{\text {elstat }}$ | $-60.4(42.8 \%)$ |
| $\Delta E_{\text {orb }}$ | $-193.9(78.5 \%)$ | $\Delta E_{\text {orb }}$ | $-80.7(57.2 \%)$ |
| $\Delta E_{\sigma}$ | $-82.82(42.7 \%)$ | $\Delta E_{\sigma}$ | $-29.9(37.1 \%)$ |
| $\Delta E_{\pi}$ | $-104.0(53.6 \%)$ | $\Delta E_{\sigma}$ | $-42.2(52.3 \%)$ |
| $\Delta E_{\text {orb }}($ rest $)$ | $-7.1(3.7 \%)$ | $\Delta E_{\text {orb }}($ rest $)$ | $-8.6(15.6 \%)$ |
| $\Delta E_{\text {dist }}$ | 1.1 | $\Delta E_{\text {dist }}$ | 0.76 |
| Energy values are given in kcal/mol. |  |  |  |

For the $\mathrm{F}_{2} \mathrm{BAlF}$ molecular, only one $\sigma$ bond existed between B and Al and both B and Al atom contribute to this $\sigma$ bond together (Figure 6d). From Figure 6b, we can observe that the occupation of the $\sigma$ 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 $\mathrm{F}_{2}$ BBF molecule, both two boron atoms have good hybridization with the s and p orbital. While for the B-Al $\sigma$ 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 3 s electrons of aluminum barely participates in bonding with other atoms and no $\pi$ bond formed in the $\mathrm{F}_{2} \mathrm{BAlF}$ molecule.

Although the $\mathrm{FBAlF}_{2}$ molecule was not observed in the experiment by the $\alpha$ - F transfer, a similar bonding composition could be demonstrated to that of $\mathrm{FBBF}_{2}$ (Figure S1). The $\mathrm{B}-\mathrm{Al}$ is also caused by the outflow of electrons (most $2 s$ electron of B ) from FB to Al , and then the ( $\mathrm{p}-\mathrm{p}$ ) $\pi$ 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 $-122.0 \mathrm{kcal} / \mathrm{mol}$ between BF and $\mathrm{AlF}_{2}$ is very strong, and $29.3 \%(-39.5 \mathrm{kcal} / \mathrm{mol})$ come from the $\sigma$ bond and $68.3 \%(-91.9 \mathrm{kcal} / \mathrm{mol})$ from $\pi$ bond; thus, compounds with $\sigma$-donor and $\pi$-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 $\mathrm{H}(\mathrm{r})=-0.12656$ 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 ( $\nabla^{2} \rho_{\mathrm{cp}}=-0.426$ ); however, this value is slightly positive $\left(\nabla^{2} \rho_{c p}=0.058\right)$ 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 $\mathrm{F}_{2} \mathrm{BM}(\mathrm{B}, \mathrm{Al})$ 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 $\mathrm{BF}_{2}$ antisymmetric and symmetric stretch mode can red-shift from 1336.9 and $1202.4 \mathrm{~cm}^{-1}$ to 1281.5 and $1180.8 \mathrm{~cm}^{-1}$.

## 4. Experimental and Computational Methods

Laser-ablated B and Al atoms react with ${ }^{11} \mathrm{BF}_{3}$ and ${ }^{10} \mathrm{BF}_{3}$ 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 ${ }^{10} \mathrm{~B}$ (Eagle Pitcher, America, $93.8 \%$ ${ }^{10} \mathrm{~B}, 6.2 \%{ }^{11} \mathrm{~B}$ ), enriched ${ }^{11} \mathrm{~B}$ (Eagle Pitcher, $97.5 \%{ }^{11} \mathrm{~B}, 2.5 \%{ }^{10} \mathrm{~B}$ ), and Al (Alfa Aesar, America, $99.999 \%$ ) atoms were reacted with ${ }^{11} \mathrm{BF}_{3}$ and ${ }^{10} \mathrm{BF}_{3}$ 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 $0.5 \mathrm{~cm}^{-1}$ between 4000 and $400 \mathrm{~cm}^{-1}$ 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 $\operatorname{CCSD}(\mathrm{T}) /$ 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 $\operatorname{CCSD}(\mathrm{T})$ [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 $\mathrm{BF}_{2}-$ MF compounds by the ORCA 4.0.1 program [32,33]. CASSCF [27] calculations including three active electrons in eight active orbitals [CAS(3e, 80)], 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 $\mathrm{BF}_{3}$ has been studied by the matrix isolation infrared spectrum and theoretical calculations. The structure and properties of the $\mathrm{B}_{2} \mathrm{~F}_{3}$ molecule, which can be drawn as $\mathrm{F}_{2} \mathrm{~B}-\mathrm{BF}$, have been investigated. The F-B-F stretching mode was located at 1336.9 and $1202.4 \mathrm{~cm}^{-1}$. For comparison, the $\mathrm{F}_{2}$ BAlF molecule was also investigated and the F-B-F stretching mode was at 1281.5 and 1180.8 $\mathrm{cm}^{-1}$. 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 $\mathrm{B}-\mathrm{B}$ and $\mathrm{B}-\mathrm{Al}$ bond in $\mathrm{F}_{2} \mathrm{BBF}$ and $\mathrm{F}_{2} \mathrm{BAlF}$ molecules. The $\mathrm{B}-\mathrm{B}$ bond in $\mathrm{F}_{2} \mathrm{BBF}$ 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, $3 s$ electrons of aluminum barely participate in bonding with other atoms, thus one bond order is formed for the $\mathrm{B}-\mathrm{Al}$ 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 $\mathrm{BF} \rightarrow \mathrm{AlF}_{2} \sigma$ donation and $\mathrm{AlF}_{2} \rightarrow \mathrm{BF} \pi$ back-donation in $\mathrm{FBAlF}_{2}$ with the associated interaction energy $\Delta \mathrm{E}_{\text {orb }}$ and charge eigenvalues $\left|v_{\mathrm{n}}\right|$ (in e).; Figure S2: Contour line diagrams of the Laplacian of the electronic density of $\mathrm{F}_{2} \mathrm{BMF}(\mathrm{M}=\mathrm{B}, \mathrm{Al})$.; Figure S3: Color-filled maps of localized orbital locator of $\mathrm{F}_{2} \mathrm{BMF}$ molecules ( $\mathrm{M}=\mathrm{B}, \mathrm{Al}$ ).; Table S1: Compositions of Natural Bond Orbitals from NBO Analysis of $\mathrm{F}_{2} \mathrm{BMF}$ molecules ( $\mathrm{M}=\mathrm{B}, \mathrm{Al}$ ); Table S2: Effective Bond Order Computed at B3LYP/def2-TZVPP level of $\mathrm{F}_{2}$ BMF molecules ( $\mathrm{M}=\mathrm{B}, \mathrm{Al}$ ); Table S3: Calculated Fundamental Frequencies of $\mathrm{F}_{2} \mathrm{BBF}$ and $\mathrm{F}_{2}$ AlBF isotopomers in the Ground ${ }^{2}$ A State.
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