

# Synthesis, Microwave Spectrum, and Structure of ArBF<sub>3</sub>, BF<sub>3</sub>CO, and N<sub>2</sub>BF<sub>3</sub>

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**Abstract:** The structures of the three species, ArBF<sub>3</sub>, N<sub>2</sub>BF<sub>3</sub>, and COBF<sub>3</sub> are reported. The species are produced by supersonic expansion. Their microwave spectra are recorded by molecular beam electric resonance spectroscopy. All three species are symmetric rotors. For ArBF<sub>3</sub> the Ar-B bond length is 3.325 (10) Å, the stretching vibration frequency is 44 (2) cm<sup>-1</sup>, and the electric dipole moment is 0.176 (2) D. For BF<sub>3</sub>CO the B-C bond length is 2.886 (5) Å, the stretching vibration frequency is 65 (8) cm<sup>-1</sup>, and the electric dipole moment is 0.592 (1) D. For N<sub>2</sub>BF<sub>3</sub> the B-N bond length is 2.875 (20) Å and the electric dipole moment is 0.35 (2) D. The three species appear to be weakly bound charge transfer complexes. An unsuccessful attempt to prepare the complex between CO and COBH<sub>3</sub> is described.

## Introduction

Boron trifluoride is widely used as a Lewis acid, so it is surprising how little detailed structural data exist for 1:1 complexes involving BF<sub>3</sub>. Such complexes are often difficult to produce in the gas phase at sufficient concentration to permit determination of their microwave spectra. In this paper we detail the synthesis and spectroscopy of three very weakly bound complexes: BF<sub>3</sub>CO, N<sub>2</sub>BF<sub>3</sub>, and ArBF<sub>3</sub>. BF<sub>3</sub> is relatively complicated in terms of classical valence structure. The elementary picture of simple sp<sup>2</sup> hybridization, single BF bonds, and a p<sub>z</sub> vacant orbital fails to account quantitatively for many of its properties. There is a similarity between diatomic BF and the BF bonds in BF<sub>3</sub>. The bond lengths are 1.266<sup>1</sup> and 1.310 Å,<sup>2</sup> respectively, while the dissociation energies are 180 and 150 kcal/mol.<sup>3</sup> Bonding in diatomic BF is well studied theoretically and shows considerable similarity to its isoelectronic partners CO and N<sub>2</sub>, in which multiple bonding is clear.<sup>4</sup> There is little doubt that the BF bonds in BF<sub>3</sub> are also multiple bonds, as has frequently been stated.<sup>5,6</sup>

A wide variety of compounds involving BF<sub>3</sub> has been studied.<sup>7</sup> While a few adducts, such as BF<sub>3</sub>C<sub>5</sub>H<sub>5</sub>N, can be distilled at high temperatures without decomposition, it is more often the case that a significant fraction of the complex is dissociated in the gas phase. Although dissociation is not a problem in structural determination by X-ray analysis, this type of data is mostly limited to complexes with a B-N bond. Hoard, Gellar, and Owen<sup>8</sup> reviewed the X-ray data for the series of molecules, BF<sub>3</sub>-NH<sub>3</sub>, BF<sub>3</sub>-MeNH<sub>2</sub>, BF<sub>3</sub>-Me<sub>3</sub>N, and BF<sub>3</sub>-MeCN. The BN bond lengths and the FBF bond angles for this series are respectively 160 Å, 111°; 1.57 Å, 110.5°; 1.59 Å, 107°; 1.64 Å, 114°. It seems that the longer BN bond lengths correlate with a BF<sub>3</sub> moiety less distorted from the planar FBF angle of 120°, i.e., weaker complexation. The BN bond length in crystalline BH<sub>3</sub>-NH<sub>3</sub> is 1.56 Å, very similar to the BF<sub>3</sub>NH<sub>3</sub> length.<sup>9</sup>

Kuczkowski and his colleagues have used microwave spectroscopy to determine B-P<sup>10</sup> and B-N<sup>11,12</sup> bond lengths for various complexes. In (CH<sub>3</sub>)<sub>3</sub>N-BF<sub>3</sub>, the B-N bond length is 1.636 Å, 0.04 Å longer than the crystal determination of Geller and Hoard.<sup>8</sup> The gas-phase B-N bond of (CH<sub>3</sub>)<sub>3</sub>N-BH<sub>3</sub><sup>12</sup> is equal to, within experimental error, that of (CH<sub>3</sub>)<sub>3</sub>N-BF<sub>3</sub>. Thus, toward complexation with trimethylamine in the gas phase or ammonia in solid phase, BF<sub>3</sub> appears to behave very similarly to BH<sub>3</sub>. Comparison of BH<sub>3</sub> and BF<sub>3</sub> as Lewis acids has been hampered by the inability to prepare and compare similar adducts, the outstanding example being carbon monoxide. While BH<sub>3</sub>CO is relatively stable and certainly stable with respect to dissociation, BF<sub>3</sub>CO has not been synthesized and structurally characterized. The purpose of the

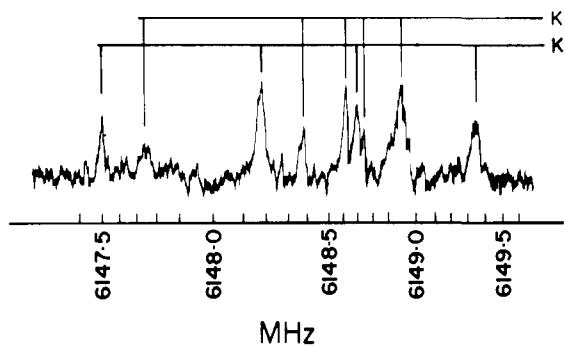
work reported here is the preparation and characterization of BF<sub>3</sub>CO. In the course of that work it was obvious that interesting comparisons could be made with other adducts to BF<sub>3</sub>. Nitrogen and argon were appealing choices, the former since it is isoelectronic to carbon monoxide. Argon appears to be a quite useful, structureless, weak Lewis base for reference.

The present work is devoted to synthesis and structural characterization of these (van der Waals) molecules. As shall be demonstrated, this structural characterization can be done with as much accuracy and to as great detail as for stable species.<sup>13-16</sup> In this sense the structural chemistry of van der Waals molecules can be as complete as that of normal stable species. The study of reactive processes involving van der Waals molecules can equally well be executed. Although the present BF<sub>3</sub> complexes have not directly been used, detailed reactive studies of van der Waals molecules have been performed by Herschbach and colleagues.<sup>17</sup> An excellent example of their work is provided by their study of the reactions involving (Cl<sub>2</sub>)<sub>2</sub>. It would appear to us that the chemistry of van der Waals molecules can be studied in as much detail as that of normal stable species, albeit by somewhat different techniques.

## Experimental Section

The BF<sub>3</sub>, Ar, CO, and N<sub>2</sub> are commercial (Matheson) and used without further purifications. To produce ArBF<sub>3</sub>, a mixture of 0.5% BF<sub>3</sub> in Ar at 600 Torr is expanded through a 0.03-mm diameter nozzle into the spectrometer. The nozzle is cooled to 170 K. Under these conditions, a large fraction of the BF<sub>3</sub> in the sample is converted to ArBF<sub>3</sub>. A larger flux of ArBF<sub>3</sub> could be obtained by using a more concentrated sample mixture. The nozzle cooling of such a mixture, however, is less efficient and the ArBF<sub>3</sub> is present in a much wider range of rotational and perhaps vibrational energy levels. Since the microwave resonances involve only the very low energy rotational states, it is useful to obtain a very cold beam by using the dilute sample mixture.

The detector for the molecular beam electric resonance spectrometer is a mass spectrometer with a high intensity space charge limited Weiss-type<sup>18</sup> electron bombardment ionizer. The beam is ionized by a high flux of rather energetic electrons (nominal acceleration potential is 130 eV). Under these conditions, ArBF<sub>3</sub> is ionized to a variety of species, the most predominant of which is BF<sub>2</sub><sup>+</sup>. Since it is necessary for a molecule to be polar to traverse the spectrometer when a wire is used to block the straight-through beam, BF<sub>2</sub><sup>+</sup> which results from ArBF<sub>3</sub> ( $\mu = 0.176$  D) can be distinguished from that resulting from ionization of BF<sub>3</sub>. Table I illustrates the results of a focusing study (focusing is the ability of a polar molecule to be focused around the beam stop by the multipole electrostatic lenses) in which the sample pressure behind the nozzle was 500 Torr. All mass peaks higher than *m/e* 89 (i.e., ArBF<sub>3</sub><sup>+</sup>, Ar<sub>3</sub><sup>+</sup>, Ar<sub>2</sub>BF<sub>2</sub><sup>+</sup>, etc.) proved to be either very weakly focusing or nonpolar. Thus it appears that polymers and copolymers other than ArBF<sub>3</sub> are at most very slightly polar. The



**Figure 1.** The  $J = 1 \rightarrow 2$  spectrum of Ar<sup>11</sup>BF<sub>3</sub> recorded at zero electric field with a 25-s time constant. To obtain all of the hyperfine components simultaneously, the spectrometer was detuned from any one transition. To obtain precise transition frequencies, each line is recorded separately.

**Table I.** Focusing Study of the ArBF<sub>3</sub> Mixture<sup>a</sup>

| <i>m/e</i> | ion                            | <i>I</i> <sub>0</sub> | <i>I</i> <sub>r</sub> | <i>I</i> <sub>r</sub> / <i>I</i> <sub>0</sub> |
|------------|--------------------------------|-----------------------|-----------------------|---|
| 49         | BF <sub>2</sub> <sup>+</sup>   | 26                    | 19                    | 0.73  |
| 68         | BF <sub>3</sub> <sup>+</sup>   | 3.9                   | 5.4                   | 1.38  |
| 89         | ArBF <sub>2</sub> <sup>+</sup> | 2.6                   | 3.0                   | 1.15  |

<sup>a</sup> *I*<sub>0</sub> = relative intensity of straight through beam; *I*<sub>r</sub> = relative intensity of beam focused around stop wire.

following observations may be deduced from Table I: (1) The mass peaks in order of decreasing *I*<sub>r</sub>/*I*<sub>0</sub> are 68 (BF<sub>3</sub><sup>+</sup>), 89 (ArBF<sub>2</sub><sup>+</sup>), and 49 (BF<sub>2</sub><sup>+</sup>). (2) The mass peaks in order of decreasing total *I*<sub>r</sub> are 49 (BF<sub>2</sub><sup>+</sup>), 68 (BF<sub>3</sub><sup>+</sup>), and 89 (ArBF<sub>2</sub><sup>+</sup>). Thus for this molecule the optimum mass spectrometer setting on which to perform spectroscopy is *m/e* 49. While not important in terms of spectroscopy, it is interesting to note that a BF<sub>3</sub><sup>+</sup> ion is more likely to result from ionization of ArBF<sub>3</sub> than BF<sub>3</sub> itself. Also, since *I*<sub>r</sub>/*I*<sub>0</sub> for *m/e* 108 (ArBF<sub>3</sub><sup>+</sup>) is very small in comparison to that of *m/e* 89 (ArBF<sub>2</sub><sup>+</sup>), it is apparent that Ar<sub>2</sub>BF<sub>3</sub> cracks frequently to give ArBF<sub>3</sub><sup>+</sup>.

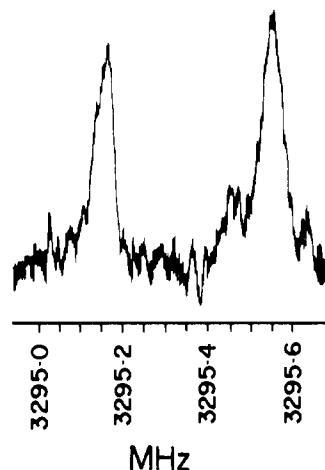
N<sub>2</sub>BF<sub>3</sub> and COBF<sub>3</sub> were obtained under similar conditions of total pressure and source temperature except that the sample mixture was 0.5% BF<sub>3</sub>, 25% CO, or N<sub>2</sub> in Ar. Ar is always the principal constituent of the mixture in order to achieve maximum cooling. With these mixtures the BF<sub>3</sub>CO or N<sub>2</sub>BF<sub>3</sub>/ArBF<sub>3</sub> ratio was always greater than 10. The fragmentation of BF<sub>3</sub>CO and N<sub>2</sub>BF<sub>3</sub> appears to be very similar to that of ArBF<sub>3</sub>. A quantitative comparison is not possible, however, owing to interference of background peaks in the mass spectrometer.

It is apparent that by use of supersonic nozzle expansion, a complex between any two constituents in the gas phase can be produced. The conditions necessary to form any particular species, however, are not always clear. During the course of the present work, an attempt was made to produce the complex between BH<sub>3</sub>CO and CO. It was hoped that this species might permit study of an interesting permutational symmetry between a chemical bond and a van der Waals bond. Two percent BH<sub>3</sub>CO (kindly prepared by Professor S. Wreford) in a CO/Ar mixture was expanded into the spectrometer and the mass spectrum was recorded. Even at this low concentration the BH<sub>3</sub>CO was observed to form large fractions of various polymers rather than simply add a second CO group. Owing to the inconvenience of working with COBH<sub>3</sub>, no further attempt to form the very interesting complex has been performed to date.

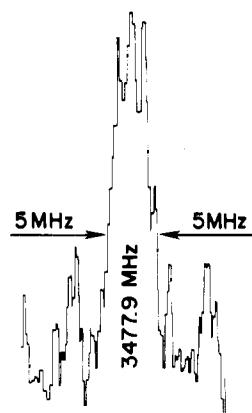
Each of the three compounds, ArBF<sub>3</sub>, BF<sub>3</sub>CO, and N<sub>2</sub>BF<sub>3</sub> is found to be a symmetric top so that the rotational energy is given by

$$E_{\text{rot}} = BJ(J+1) - (A - B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 + f(IJK) \quad (1)$$

where *f*(*I*, *J*, *K*) is the hyperfine energy due to the presence of one or more nuclear electric quadrupole couplings. Since the selection rules are  $\Delta J = 0 \pm 1$ ,  $\Delta K = 0$ ,  $B$ ,  $D_J$ , and  $D_{JK}$  can be determined from the microwave spectrum. For ArBF<sub>3</sub> and BF<sub>3</sub>CO, in which the only nuclear quadrupole is in the boron atom, the hyperfine structure was resolved and analyzed to give the boron nuclear electric quadrupole



**Figure 2.** The  $J = 1 \rightarrow 0$   $F = \frac{3}{2} \rightarrow \frac{3}{2}$  spectrum of BF<sub>3</sub><sup>12</sup>CO recorded at 295.3 V/cm with a 25-s time constant.



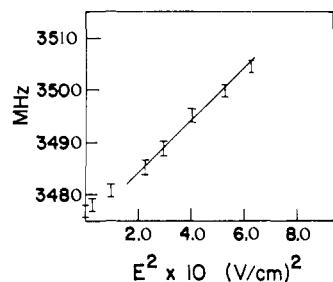
**Figure 3.** A computer averaged plot of the  $J = 1 \rightarrow 0$  transition of N<sub>2</sub>BF<sub>3</sub> in which the oscillator is broadened with white noise in order to mask the complex hyperfine structure. The electric field is 492.1 V/cm and the spectrum was averaged for 20 min.

coupling constant, *eqQ*. In the case of N<sub>2</sub>BF<sub>3</sub> three nuclear quadrupoles are present and the hyperfine structure is expected to be complex. For this molecule the hyperfine splittings were intentionally not resolved and only the *B* rotational constant was measured. The rotational transitions for each of the three complexes were measured with various applied electric fields in order to obtain the dipole moments for the three species.

Although radio-frequency spectra have previously been recorded for ArBF<sub>3</sub>,<sup>19</sup> no attempt is made to analyze such spectra in this paper. The difficulty in unambiguously assigning the quantum numbers of the Stark spectrum of a symmetric top appears severe. This difficulty is nonexistent for microwave spectra involving changes in rotational energy. The latter spectra can provide all the molecular structural information; thus, analysis of the radio-frequency spectra was not pursued.

For ArBF<sub>3</sub> and BF<sub>3</sub>CO, the  $J = 1 \rightarrow 2$  and  $J = 1 \rightarrow 0$  microwave transitions were both recorded along with the concomitant hyperfine structure with a resolution of 20 kHz. The  $J = 1 \rightarrow 2$  spectrum of ArBF<sub>3</sub> is shown in Figure 1. Figure 2 shows the  $J = 1 \rightarrow 0$ ,  $F = \frac{3}{2} \rightarrow \frac{3}{2}$  transition for BF<sub>3</sub>CO with a 300 V/cm electric field. Both of these spectra were recorded with a 25-s time constant. In Figure 1 the spectrometer focusing fields are detuned for any given line so that all of the lines would be visible on a single scan. As mentioned above, the hyperfine structure of N<sub>2</sub>BF<sub>3</sub> rotational transitions is expected to be exceedingly complex. To mask this structure the oscillator line width was broadened to 5 MHz. A recording of the  $K = 0$ ,  $M_J = 0$ ,  $J = 1 \rightarrow 0$  transition at 500 V/cm with the broadened oscillator is shown in Figure 3. Higher frequency rotational transitions for each species were measured with noise broadened radiation.

Both the <sup>10</sup>B and <sup>11</sup>B isotopic species were studied for each complex; for BF<sub>3</sub>CO, <sup>13</sup>C substitution was also used (using 90% enriched CO).



**Figure 4.** The Stark effect of the  $K = 0, J = 1, M_J = 0 \rightarrow J = 0$  line of  $\text{N}_2\text{BF}_3$ .

**Table II.** Zero-Field Transitions Measured for  $\text{ArBF}_3$

| frequency, MHz              | $J$ | $J'$ | $F$   | $F'$  | $K$  |
|-----------------------------|-----|------|-------|-------|------|
| $\text{Ar}^{11}\text{BF}_3$ |     |      |       |       |      |
| 15 361.0 (2.0)              | 5   | 4    |       |       |      |
| 12 289.0 (2.0)              | 4   | 3    |       |       |      |
| 9220.0 (2.0)                | 3   | 2    |       |       |      |
| 6149.355 (20)               | 2   | 1    | $5/2$ | $5/2$ | 0    |
| 6148.946 (10)               | 2   | 1    | $5/2$ | $3/2$ | 1    |
| 6148.685 (10)               | 2   | 1    | $5/2$ | $3/2$ | 0    |
| 6148.62 (3)                 | 2   | 1    | $5/2$ | $5/2$ | 1    |
| 6148.38 (3)                 | 2   | 1    | $1/2$ | $3/2$ | 1    |
| 6148.195 (20)               | 2   | 1    | $3/2$ | $3/2$ | 0    |
| 6147.774 (10)               | 2   | 1    | $1/2$ | $1/2$ | 1    |
| 6147.520 (10)               | 2   | 1    | $1/2$ | $3/2$ | 0    |
| 3075.025 (25)               | 1   | 0    | $3/2$ | $3/2$ | 0    |
| $\text{Ar}^{10}\text{BF}_3$ |     |      |       |       |      |
| 9265 (2)                    | 3   | 2    |       |       |      |
| 6178.40 (3)                 | 2   | 1    | 4     | 3     | 1    |
| 6178.36 (3)                 | 2   | 1    | 3     | 3     | 1    |
| 6177.88 (3)                 | 2   | 1    | 5     | 4     | 0    |
| 6177.78 (3)                 | 2   | 1    | 4     | 3     | 0    |
| 6177.62 (3)                 | 2   | 1    | 3, 3  | 2, 3  | 1, 0 |
| 6177.25 (3)                 | 2   | 1    | 2     | 2     | 1    |
| 6176.91 (3)                 | 2   | 1    | 1, 2  | 2, 3  | 1, 0 |
| 3089.980 (25)               | 1   | 0    | 3     | 3     | 0    |

Tables II, III, and IV list the microwave transition frequencies for each species at zero electric field. Tabulations of line frequencies as a function of applied electric field are lengthy and are given elsewhere.<sup>20</sup>

## Results

The spectral lines listed in Tables II, III, and IV can each be fit to within experimental error using the symmetric top Hamiltonian (eq 1) and including the boron hyperfine splittings to first-order perturbations of the rotational energy. The Stark data were fitted with the program of Harris<sup>21</sup> in which the Hamiltonian is diagonalized in an  $|I, J, F, M_F\rangle$  basis set. The dipole moment of  $\text{N}_2\text{BF}_3$  was measured to 5% precision from the broadened measurement of the  $J = 1 \rightarrow 0$  transition at electric fields of up to 2500 V/cm. Above  $E = 1500$  V/cm the Stark effect of this transition is independent of the hyperfine splittings and quadratic in electric field. Thus, the dipole moment of the complex can be calculated directly from the least-squares fit to the transition frequency vs.  $E^2$  plot shown in Figure 4.

The spectroscopic constants obtained for each of the species studied are listed in Table V. The number in parentheses is a conservatively large error estimate for the least significant figures of each constant. It is important to note that the constants are based on high-precision measurement of low  $J$  lines. Both the hyperfine structure constants (for  $\text{ArBF}_3$  and  $\text{BF}_3\text{CO}$ ) and the dipole moments for each complex are unambiguously determined.

**Table III.** Observed Zero-Field Transitions for  $\text{BF}_3\text{CO}$  (MHz)

| $J$ | $J'$ | A. Low Resolution                |                                  |                                  |
|-----|------|----------------------------------|----------------------------------|----------------------------------|
|     |      | $^{11}\text{BF}_3^{12}\text{CO}$ | $^{10}\text{BF}_3^{12}\text{CO}$ | $^{11}\text{BF}_3^{13}\text{CO}$ |
| 7   | 6    | 23 071 (10)                      |                                  |                                  |
| 6   | 5    | 19 768 (10)                      |                                  |                                  |
| 5   | 4    | 16 465 (4)                       |                                  | 16 527 (8)                       |
| 3   | 2    | 9882 (8)                         |                                  |                                  |

| $J$                              | $J'$ | $K$ | B. High Resolution |       |                                  |
|----------------------------------|------|-----|--------------------|-------|----------------------------------|
|                                  |      |     | $F$                | $F'$  | $^{11}\text{BF}_3^{12}\text{CO}$ |
| 2                                | 1    | 0   | $5/2$              | $5/2$ | 6588.355 (10)                    |
| 2                                | 1    | 1   | $5/2$              | $3/2$ | 6588.127 (10)                    |
| 2                                | 1    | 1   | $3/2$              | $3/2$ | 6587.92 (3)                      |
| 2                                | 1    | 0   | $3/2$              | $5/2$ | 6587.880 (10)                    |
| 2                                | 1    | 1   | $5/2$              | $5/2$ | 6517.15 (3)                      |
| 2                                | 1    | 0   | $5/2$              | $3/2$ | 6587.665 (10)                    |
| 2                                | 1    | 1   | $3/2$              | $5/2$ | 6587.56 (3)                      |
| 2                                | 1    | 1   | $3/2$              | $1/2$ | 6587.28 (3)                      |
| 2                                | 1    | 0   | $3/2$              | $3/2$ | 6587.170 (10)                    |
| 2                                | 1    | 1   | $1/2$              | $1/2$ | 6586.915 (10)                    |
| 1                                | 0    | 0   | $3/2$              | $3/2$ | 3294.460 (15)                    |
| $^{10}\text{BF}_3^{12}\text{CO}$ |      |     |                    |       |                                  |
| 2                                | 1    | 0   | 4                  | 4     | 6612.82 (3)                      |
| 2                                | 1    | 1   | 3                  | 3     | 6612.46 (3)                      |
| 2                                | 1    | 0   | 4                  | 3     | 6611.70 (3)                      |
| 1                                | 0    | 0   | 3                  | 3     | 3306.876 (15)                    |
| $^{10}\text{BF}_3^{13}\text{CO}$ |      |     |                    |       |                                  |
| 3271.70 (3)                      |      |     |                    |       |                                  |

**Table IV.** Observed Zero-Field Resonances for  $\text{N}_2\text{BF}_3$  (MHz)

| $J$ | $J'$ | $\text{N}_2^{11}\text{BF}_3$ | $\text{N}_2^{10}\text{BF}_3$ |
|-----|------|------------------------------|------------------------------|
| 5   | 4    | 17 370 (3)                   | 17 434 (3)                   |
| 4   | 3    | 13 898 (3)                   |                              |
| 1   | 0    | 3477.2 (20)                  |                              |

## Structural Interpretation

The symmetric top spectrum of each complex clearly establishes the structure as that of Ar,  $\text{N}_2$ , or CO adding along the symmetry axis of the  $\text{BF}_3$  constituent. The formation of a complex in general might be expected to alter the monomeric structures of the compounds. No change in the CO or  $\text{N}_2$  bond lengths is expected, however, on the basis of the structure of  $\text{BH}_3\text{CO}^{22,23}$  where the CO bond length is  $1.135 \pm 0.010 \text{ \AA}$  compared to  $1.131 \text{ \AA}$  ( $r_0$ ) in carbon monoxide. As discussed above, the B-F bonds in  $\text{BF}_3$  are similar to the triply bonded BF radical. It is expected that any electron transfer to  $\text{BF}_3$  would result in lengthened B-F bonds. In this analysis any bond-length change is also assumed to be negligible because of the very weak bonding interaction and because the spectroscopic measurements are relatively insensitive to the B-F bond length. Given the above assumptions, a fairly complete structure determination can be performed in the case of  $\text{BF}_3\text{CO}$ . First, since isotopic substitution is available at both the carbon and boron atoms, the C-B distance can be determined independently of other structural assumptions by using the method developed by Kraitchman.<sup>24</sup> Using rotational constants for the four isotopically substituted species, four values for the C-B separation are obtained: 2.885, 2.886, 2.886, and 2.888 Å. Next, the symmetric top structure consistent with the four measured rotational constants must be found. Two variables can be varied for this purpose: (1) the oxygen position, (2) the C-B-F structural angle. The oxygen could be either between the carbon and boron atoms or away from the boron atom. No value of the C-B-F angle and the 2.886 Å C-B separation is consistent with the measured rotational constant for the former possibility. Thus, it must be concluded that the carbon bonds directly to the boron with the oxygen pointed

**Table V.** Spectroscopic Constants for ArBF<sub>3</sub>, BF<sub>3</sub>CO, and N<sub>2</sub>BF<sub>3</sub>

| molecule                                       | <i>B</i> <sub>0</sub> , MHz | <i>D</i> <sub>J</sub> , kHz | <i>D</i> <sub>JK</sub> , kHz | <i>eqQ</i> , MHz | $\mu$ , D |
|--|-----------------------------|-----------------------------|------------------------------|------------------|-----------|
| Ar <sup>11</sup> BF <sub>3</sub>               | 1537.261 (10)               | 9.6 (1.0)                   | 74 (10)                      | 2.70 (5)         | 0.176 (2) |
| Ar <sup>10</sup> BF <sub>3</sub>               | 1544.586 (10)               |                             |                              | 5.64 (10)        | 0.176 (2) |
| <sup>11</sup> BF <sub>3</sub> <sup>12</sup> CO | 1646.961 (10)               | 3.8 (1.0)                   | 26 (10)                      | 2.75 (5)         | 0.592 (1) |
| <sup>10</sup> BF <sub>3</sub> <sup>12</sup> CO | 1653.015 (10)               |                             |                              | 5.74 (10)        | 0.592 (1) |
| <sup>11</sup> BF <sub>3</sub> <sup>13</sup> CO | 1629.301 (15)               |                             |                              |                  | 0.592 (2) |
| <sup>10</sup> BF <sub>3</sub> <sup>13</sup> CO | 1635.426 (15)               |                             |                              |                  |           |
| N <sub>2</sub> <sup>11</sup> BF <sub>3</sub>   | 1737.0 (1.0)                |                             |                              |                  | 0.35 (2)  |
| N <sub>2</sub> <sup>10</sup> BF <sub>3</sub>   | 1743.5 (1.0)                |                             |                              |                  |           |

outward. For the four isotopic species, this results in C-B-F angles of 90.34, 90.37, and 90.41°, well within the limits of self-consistency. Since each substituted atom in the Kraitchman analysis is over 1 Å from the center of mass, the 2.886 *r*<sub>s</sub> bond length is probably identical with the best *r*<sub>0</sub> value.

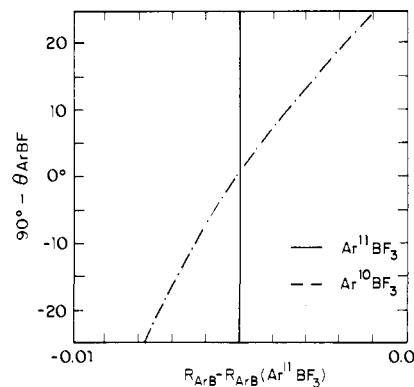
It is of interest to roughly determine the effect of our approximations to determine error limits for structure analysis. Given the extremely limited data available for polyatomic van der Waals molecules, it is somewhat speculative to discuss the effects of anharmonicity, zero-point motion, and constituent relaxation upon complexation. Triatomic species have been studied in great detail.<sup>13,14</sup> Even for a very wide amplitude bender like ArHCl, the harmonic, semirigid model yields a rather accurate representation of the bottom of the potential well. Thus, it seems reasonable to estimate error limits due to zero point motion from a harmonic approximation. There are five modes of motion associated with the weak bond of BF<sub>3</sub>CO, one stretching mode and two doubly degenerate bending modes. The effect of the stretching mode is simply that an *r*<sub>0</sub> (or *r*<sub>s</sub>) value for the weak bond length is determined rather than *r*<sub>e</sub>. In the case of the linear triatomic molecule ArClF, which probably is more weakly bound than BF<sub>3</sub>CO, *r*<sub>e</sub> is 0.05 Å shorter than *r*<sub>0</sub>.<sup>13</sup> The bending vibrations lead to zero-point angular averaging which can affect the structure determination. For instance, a first approximation to the normal mode with the lowest effective mass and thus highest effective angular dispersion is the bending of the linear B-C-O group. Assigning the entire BF<sub>3</sub> mass to the boron position and assuming that the force constant is equal to that of ArClF<sup>13</sup> (0.02 mdyn Å) the zero point averaged angle for this motion is 4°. Using this value for the B-C-O angle in the C-B-F angle calculation changes the result by only 0.08°. Finally, we consider the error that could be introduced by expansion of the B-F bond length upon complex formation. Because the BF<sub>3</sub> unit remains so nearly planar, such expansion is expected to be slight. Even if the length increased from 1.310 to 1.330 Å, however, the structural angle would only change from 90.65 to 90.35°. In summary, the structural parameters for BF<sub>3</sub>CO are judged to be *r*<sub>0</sub> = 2.886 ± 0.005 Å for the B-C bond,  $\theta_{CBF}$  = 90.65 ± 0.25°.

The structure determination for ArBF<sub>3</sub> is much less precise if only the two rotational constants (<sup>10</sup>B, <sup>11</sup>B) are used. The criterion for a determination in this sense is simply that the two isotopic species have the same structure. Figure 5 illustrates the ensemble of Ar-B bond lengths and ArB-F bond angles which are consistent with the two measured rotational constants. Based on this plot the best value for *r*<sub>0</sub> is 3.34 Å while  $\theta$  is 89.5°. Consideration of the error limits of this determination shows that they are considerable. Because of zero-point averaging, it is not reasonable to expect the two bond lengths to be equal to a higher precision than  $5 \times 10^{-4}$  Å. Figure 5 shows that this limits the angular determination to within ±1.5°. Finally,  $\Delta r/\Delta\theta$  at  $\theta = 90^\circ$  is 0.02 Å/deg, so that the structural values from this argument are *r*<sub>0</sub> = 3.34 ± 0.03 Å,  $\theta = 89.5 \pm 1.5^\circ$ . A simple physical argument can be used to narrow the range of the determination. Since chemical intuition and the dipole moment measurement both indicate

**Table VI.** Structural Parameters for ArBF<sub>3</sub>, N<sub>2</sub>BF<sub>3</sub>, and BF<sub>3</sub>CO<sup>a</sup>

| molecule                       | <i>R</i> <sub>B-D</sub> , Å | $\theta_{DBF}$ | $\theta_{FBF}$ |
|--------------------------------|-----------------------------|----------------|----------------|
| ArBF <sub>3</sub>              | 3.325 (10)                  | 90.5 (5)       | 120            |
| N <sub>2</sub> BF <sub>3</sub> | 2.875 (20)                  | 90.5 (5)       | 120            |
| BF <sub>3</sub> CO             | 2.886 (5)                   | 90.65 (25)     | 119.98         |

<sup>a</sup> D = donor atom. Error limit of the least significant figures given in parentheses.

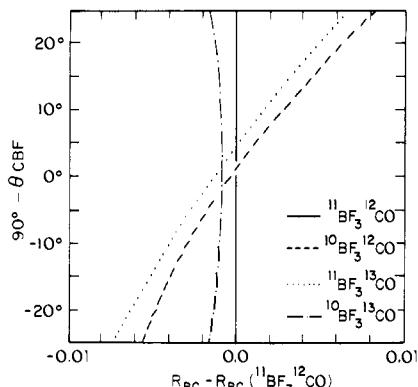


**Figure 5.** The ensemble (*R*<sub>ArB</sub>,  $\theta_{ArBF}$ ) which is consistent with the measured rotational constant of Ar<sup>10</sup>BF<sub>3</sub> and Ar<sup>11</sup>BF<sub>3</sub>. The structure of the complex is given by the intersection of two lines. Error limits for this type of determination are discussed in the text.

strongly that the BF<sub>3</sub> unit is less distorted in ArBF<sub>3</sub> than BF<sub>3</sub>CO, it is clear that the Ar-B-F angle must be within 90 ± 1°. Secondly, it is highly unlikely that the fluorine atoms bend toward the Ar. This limits the structural angle to 90.5 ± 0.5°. Given this reasonable limitation of the structural angle, agreement with the rotational constant limits the bond length to be 3.325 ± 0.010 Å. These values are well within the limits of the graphical determination. It is interesting to note that the graphical structure determination for BF<sub>3</sub>CO with four isotopic measurements as illustrated in Figure 6 would also lead to a rather imprecise structure determination with the C-B-F structural angle less than 90° but with error limits that easily span the more precise determination given above.

Because the hyperfine structure of BF<sub>3</sub>N<sub>2</sub> was not resolved, the structure of this molecule is determined less precisely than that of ArBF<sub>3</sub>. The graphical determination shown in Figure 7 illustrates the error limits involved in the experimental uncertainty. Undoubtedly, however, the physical arguments used to limit the ArB-F angle to being 90 ± 0.5° also apply to N<sub>2</sub>BF<sub>3</sub>. Thus, agreement with the rotational constants limits the B-N bond length to be 2.875 ± 0.020 Å.

We gain further insight into the nature of the van der Waals bond in these systems from analysis of the centrifugal distortion constant *D*<sub>J</sub>. For its analysis we consider that all nonrigidity of the complex arises from the van der Waals bond. The constant *D*<sub>J</sub> then provides the stretching force constant, or vibration frequency.<sup>25</sup> From the values of 9.6 (1.0) kHz in ArBF<sub>3</sub> and 3.8 (1.0) kHz in COBF<sub>3</sub>, we obtain, in following Kivelson



**Figure 6.** The ensemble ( $R_{CB}$ ,  $\theta_{CBF}$ ) which is consistent with the rotational constants of the four isotopic species of  $BF_3CO$  which were studied. Since the isotope effect of carbon substitution is small, the accuracy of this structure determination is best judged by comparing the intersections of each pair of lines with a common carbon isotope. On this basis the structural angle would be determined to be  $89 \pm 2^\circ$ .

and Wilson, the stretching frequency and force constant  $44 \pm 2 \text{ cm}^{-1}$  and  $0.029 \pm 0.003 \text{ mdyn}/\text{\AA}$  for  $ArBF_3$  and  $65 \pm 8 \text{ cm}^{-1}$  and  $0.050 \pm 0.013 \text{ mdyn}/\text{\AA}$  for  $COBF_3$ .

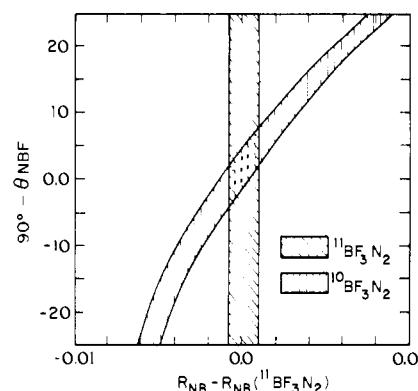
## Discussion

The present results are in most ways in good accordance with anticipation. That  $BF_3$  and CO do not interact strongly is known from the numerous failures to prepare this complex by classical methods. The B-C observed bond lengths in  $BH_3CO$  and  $BF_3CO$  differ by almost a factor of 2. The bond stretching force constants of 2.63 ( $BH_3CO$ ) and  $0.05 \text{ mdyn}/\text{\AA}$  ( $BF_3CO$ ) differ by two orders of magnitude. In the present work we do not obtain an independent determination of the bond dissociation energy for  $BF_3CO$ .

The similarity in structure of the three species,  $BF_3CO$ ,  $N_2BF_3$ , and  $ArBF_3$ , is that expected for a donor-acceptor picture of the binding. Clearly, Ar, N<sub>2</sub>, and CO act as  $\sigma$  donors. Of the three, argon is the poorest Lewis base. While we did not obtain a value for the bond stretching force constant in  $N_2BF_3$ , it is likely from the similarity in the donor-acceptor separations in  $N_2BF_3$  and  $COBF_3$  that the force constants will also be similar. The closest analogue,  $N_2BH_3$ , has not been prepared or studied as far as we are aware. Some comparisons, however, may be obtained by considering the isoelectronic (to  $BH_3CO$ ) species  $CH_2N_2$  (diazomethane) and  $CH_2CO$  (ketene). The CN bond length is 1.300 Å while the CC bond length is 1.314 Å. This difference of 0.014 Å has the same sign and is of the same magnitude as the difference observed between  $N_2BF_3$  and  $COBF_3$  if our assumptions about the  $BF_3$  subunit are correct. As discussed in the previous section, the observed distortion from planarity of the  $BF_3$  component is quite small in  $ArBF_3$  and  $BF_3CO$ . This distortion of  $<1^\circ$  could be an artifact of our analysis, although qualitative consideration of the effect, upon rotational constants, of the other, ignored, degrees of freedom does not lead to a large effect.

Of special interest is  $ArBF_3$ . The Ar-B bond length of 3.325 Å and stretching force constant of 0.030 mdyn/Å are virtually identical with those of Ar-Cl in  $ArClF$ . This similarity in structural parameters appears to extend to the electronic structure as well. The dipole moment of  $ArBF_3$  is 0.176 D. This is identical with the increase in dipole moment of  $ArClF$  over  $ClF$ , 0.175 D.<sup>13</sup>

The Ar-B bond length observed is apparently that expected. First, the "van der Waals" radius of argon is generally assumed to be identical with its periodic table neighbor chlorine. From studies of boron chloride systems, Lipscomb et al.<sup>26</sup> give 3.30–3.35 Å as reasonable van der Waals contacts for B-Cl.



**Figure 7.** The ensemble ( $R_{NB}$ ,  $\theta_{NBF}$ ) which is consistent with the measured  $B_0$  of  $N_2BF_3$ . The width of the plots indicates the experimental uncertainty due to the use of an artificially broadened oscillator (see Figure 3).

We note that in  $Cl_2$  crystal, the nearest Cl-Cl nonmolecular distance is 3.34 Å. Thus, the observed Ar-B distance is quite consistent in spite of the complexity of bonding in  $BF_3$ .

There are at present very little structural data for extremely weak complexes of CO and N<sub>2</sub>. The observed 0.4 Å difference between  $ArBF_3$  and  $COBF_3$  and  $N_2BF_3$  may then be useful in estimating separations in other weak complexes of CO and N<sub>2</sub>. It will be interesting to see how uniform this difference is in other complexes.

The electric dipole moments of these complexes give some indication of the charge redistribution that occurs in forming even extremely weak bonds. The estimation of the dipole moment of a complex from considerations of the charge distributions and polarizabilities of the molecular components appears to be exceedingly difficult. At the equilibrium separation, the electron distribution in the separate molecular components overlaps. Since these are closed-shell systems, a complex redistribution is required by the Pauli principle. Models of distortion which assume that the mutual electric fields of molecular components may be regarded as externally applied without regard to the electron structure of the subsystems ignore the Pauli principle. It is unclear that the computed dipolar distortions of such models are physically meaningful.

In a more empirical manner, the observed value of the dipole moment of  $ArBF_3$  is in reasonable accord with the model of a quadrupole induced dipole. The large value of the dipole moment of  $BF_3CO$  cannot be accounted for by this model, nor can that of  $N_2BF_3$ .<sup>20</sup>

In discussing the geometry of these complexes it was shown that the rotational constants are consistent with a  $<1^\circ$  distortion of the  $BF_3$  plane. The dipole moment derivative for the A<sub>2</sub> out of plane bending motion is determined to be 0.09 D/deg.<sup>29,30</sup> Thus, it is not possible to account for the dipole moments of the three complexes in terms of this distortion.

One further indicator of charge distribution in these complexes is the boron nuclear quadrupole coupling constant. Within experimental error  $eqQ^{11}_B$  is identical in  $COBF_3$ ,  $ArBF_3$ , and  $BF_3$  solid.<sup>31,32</sup> Unfortunately, this observation is not extremely useful, owing to the unknown magnitudes of zero-point oscillation in both the complexes and  $BF_3$  solid. It must be noted that the present measurement is the vibrational averaged quantity along the symmetry axis. Unfortunately, we do not have any independent determination of the bending amplitudes in  $ArBF_3$  and  $COBF_3$ . The boron nuclear quadrupole coupling constant in free  $BF_3$  has not been determined owing to the lack of dipole moment. Comparison of values of the coupling constant in complexes with that in the solid does not provide much insight into either vibrational amplitudes or charge redistribution.

It will be of considerable interest to provide an adequate

electron structure characterization of these complexes. An attempt to calculate stable structures for ArBF<sub>3</sub> and COBF<sub>3</sub> failed.<sup>32</sup> In this attempt, incorrect geometries were assumed. The present results provide precision geometries which should be useful in eliminating the need for geometry variation. Such calculations provide a very demanding test for the validity of quantum mechanical calculations. A double  $\zeta$  calculation using the correct geometry for ArBF<sub>3</sub> yields a repulsive potential.<sup>33</sup> Similar calculations for N<sub>2</sub>BF<sub>3</sub> and BF<sub>3</sub>CO gave binding energies of about 4 kcal/mol, but also yield dipole moments quite different from those measured. It seems very important to us that the discrepancy between experiment and theory be more completely understood. This is especially true in light of the fact that extensive computer modeling of van der Waals systems (i.e., physisorption, liquid and macromolecule dynamics) is being performed.

## Summary

The present work is intended to demonstrate several points. First, it is clear from these and a large number of similar experiments utilizing adiabatic expansion that virtually any binary complex may be readily synthesized. Secondly, unambiguous structural analysis by high-resolution spectroscopy is relatively straightforward for polar species or species whose fluorescence can be excited by tunable lasers.<sup>16</sup> Thus, the nature of the interaction between virtually any pair of molecules can be experimentally elucidated.

The present species in our view show that there is no abrupt change between weak and strong molecular interactions. The extension of the series ArBF<sub>3</sub>, N<sub>2</sub>BF<sub>3</sub>, and COBF<sub>3</sub> toward very strongly bound species, such as NH<sub>3</sub>BF<sub>3</sub>, appears perfectly feasible, with little present reason to expect any dramatic discontinuity. Systems such as NaAr, Ar<sub>2</sub>, and HClAr appear to be much more weakly bound than ArBF<sub>3</sub>. This continuity in bonding is further seen by the relatively large electron redistribution that occurs in the BF<sub>3</sub> complexes. The large electric dipole moment of BF<sub>3</sub>CO shows that even at a separation of 3 Å, considerable charge redistribution occurs.

The difference between BF<sub>3</sub> and BH<sub>3</sub> as Lewis acids is only superficially explored by the present work. It appears that the earlier concepts of BF<sub>3</sub> having multiple bonding and therefore not being electron deficient in the planar configuration are well borne out by this work. It would be extremely interesting to explore the binding of the inert gases with BH<sub>3</sub> to see whether

poor Lewis bases such as argon or xenon both bind well to and induce nuclear distortions in BH<sub>3</sub>.

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