# High Resolution Fourier Transform Infrared Spectra of <sup>10</sup>B-Labelled BF<sub>3</sub>

EDUARD ZEISBERGER<sup>1,2,3</sup> AND ANDREAS RUOFF

Sektion Schwingungsspektroskopie, Universität Ulm, D-7900 Ulm, West Germany

The infrared spectra of the  $v_2$ ,  $v_3$ ,  $v_4$ ,  $v_1 + v_4$  and  $2v_2 - v_2$  bands of isotopically enriched trifluoroborane (95% <sup>10</sup>BF<sub>3</sub>) have been measured by means of a Fourier transform spectrometer with a resolution of about 0.004 cm<sup>-1</sup>. A total of about 12 500 rovibrational transitions have been assigned. The shifts of the K'' = 3 transitions due to the splitting operators  $\hat{h}_{06}$  and  $\hat{h}_{24}$  have been observed for the  $v_3$ ,  $v_4$ , and  $v_1 + v_4$  bands. Ground state constants and parameters for the excited states  $v_2 = 1$ ,  $v_3 = 1$ ,  $v_4 = 1$ , and  $v_2 = 2$  have been improved. The parameters for the excited state  $v_1 = v_4 = 1$  have been obtained for the first time. Moreover, the splitting constants  $\Delta_3^0$ ,  $t_3$ ,  $t_4$ ,  $t_{14}$ , and their signs have been determined unambiguously. Spectroscopic constants for the  $v_1 = 1$  state have been deduced as well as the constants  $x_{22}$ ,  $\eta_{14}$ ,  $B_e$ , and  $C_e$ . (© 1989 Academic Press, Inc.

#### I. INTRODUCTION

Natural BF<sub>3</sub> consists of the two isotopomers <sup>10</sup>BF<sub>3</sub> (19.8%) and <sup>11</sup>BF<sub>3</sub> (80.2%). Both are planar molecules which belong to the group  $D_{3h}(M)^4$ . They have no permanent dipole moments in their nonrotating ground vibrational states. Hence, highresolution IR and Raman spectroscopy and/or double-resonance methods are important to obtain information not only about the molecular constants of the excited vibrational states but also about the ground vibrational state parameters.

Twenty years ago for the first time the IR spectra of the isotopically enriched isotopomers of BF<sub>3</sub> were studied with medium resolution (about 0.05 cm<sup>-1</sup>) by the group of Ginn and Overend (1-3). They determined various molecular parameters including the rotational constant  $B_0$  for <sup>10</sup>BF<sub>3</sub> and <sup>11</sup>BF<sub>3</sub>. Moreover,  $B_0$  was redetermined for <sup>11</sup>BF<sub>3</sub> by rotational Raman spectroscopy (4). However, due to the moderate resolution available the accuracy of all these molecular constants was limited.

Recently Yamamoto, Kuchitsu, and coworkers studied the infrared spectra of trifluoroborane in natural isotopic abundance (5-8). The spectra were recorded in the spectral region of the  $v_2$  and  $v_3$  band with Doppler-limited resolution by using a tunable diode laser spectrometer. For both isotopomers between 400 and 700 lines were assigned for each of the  $v_2$ ,  $v_2 + v_4 - v_4$ , and  $v_3$  bands, as well as about 200 lines for each of the  $2v_2 - v_2$  and  $v_2 + v_1 - v_1$  bands. By means of IR-MW double-resonance experiments

<sup>&</sup>lt;sup>1</sup> Part of the author's dissertation, Universität Ulm, 1987.

<sup>&</sup>lt;sup>2</sup> Present address: Hoechst AG, Analytisches Labor G 865, D-6230 Frankfurt 80.

<sup>&</sup>lt;sup>3</sup> Partly presented at the Tenth Colloquium on High Resolution Molecular Spectroscopy, Dijon, September 14–18, 1987.

<sup>&</sup>lt;sup>4</sup> As usual the label (M) designates a molecular symmetry group.

TABLE	I
-------	---

Band	Range [cm <sup>-1</sup> ]	Pressure [mbar]	Scans	S/N	Resolution (FWHM) [cm <sup>-1</sup> ]	Wavenumber Standard ( <u>13,14</u> )
$\left[\frac{v_2}{2v_2-v_2}\right]$	645 -775	1;3	160	100:1	0.0035	CO2
V <sub>3</sub>	1430 -1570	1	50	80:1	0.0035	H <sub>2</sub> O
V4	425 -555	3	160	50:1	0.0035	CO2
$v_1 + v_4$	1320 -1420	4	120	120:1	0.0048	H <sub>2</sub> O

Experimental Details of the Infrared Spectra of <sup>10</sup>BF<sub>3</sub>

these authors observed, additionally, pure rotational transitions in the  $v_3 = 1$  state for both isotopomers and in the ground vibrational state for <sup>10</sup>BF<sub>3</sub>. The combined analysis of all these rovibrational and pure rotational transitions improved the molecular parameter sets of the  $v_2 = 1$ ,  $v_3 = 1$ , and  $v_4 = 1$  states and of the ground vibrational state for the <sup>10</sup>BF<sub>3</sub> and <sup>11</sup>BF<sub>3</sub>. Oldani and Bauder (9) completed the evaluation of the ground vibrational state constants of <sup>11</sup>BF<sub>3</sub> by observing pure rotational transitions in the ground vibrational state of this isotopomer.

In order to overcome the disadvantages of diode laser spectrometers (e.g., no continuous sweeping over wide spectral ranges and low absolute wavenumber accuracy) and also to obtain more precise spectroscopic constants for <sup>10</sup>BF<sub>3</sub> and <sup>11</sup>BF<sub>3</sub>, the infrared spectra of isotopically enriched (about 95%) samples were investigated with a resolution of about 0.004 cm<sup>-1</sup> by means of a Fourier transform spectrometer (10).

In this paper we report the analysis of the  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_1 + \nu_4$ , and  $2\nu_2 - \nu_2$  bands of <sup>10</sup>BF<sub>3</sub>. The results for the corresponding bands of isotopically enriched <sup>11</sup>BF<sub>3</sub> will be published elsewhere (11).

## **II. EXPERIMENTAL DETAILS**

 $^{10}$ BF<sub>3</sub> was prepared at room temperature by the fluorination of isotopically labelled boric acid (Hempel GmbH, Düsseldorf; 95%  $^{10}$ B) with fluorosulfonic acid (12). The raw product was purified by a trap to trap condensation in vacuo. The yield was about 75%. No impurities could be detected by infrared spectroscopy.

The spectra<sup>5</sup> were recorded in vacuo by means of a prototype of the interferometer BRUKER IFS 120 HR (10). It was equipped with a Ge/KBr beam splitter, a MCT detector for the 1000–1600 cm<sup>-1</sup> range, and a Cu-doped Ge detector for the region 420–800 cm<sup>-1</sup>. The optical path difference was 350 cm and a trapezoidal apodization function was applied. The effective resolution (FWHM) and further experimental details are listed in Table I. Two stainless steel cells, 11 cm and 22 cm long, with KBr

<sup>&</sup>lt;sup>5</sup> Lists of observed and calculated wavenumbers (120 pp.) as well as the correlation matrices have been deposited in the Sektion Spektren- und Strukturdokumentation, Universität Ulm, P.O. Box 4066, D-7900 Ulm (Dr. J. Vogt).

windows were employed. Calibration was done with lines of H<sub>2</sub>O and of CO<sub>2</sub> (13. 14), the absolute accuracy of which was between  $1 \times 10^{-3}$  cm<sup>-1</sup> and  $1 \times 10^{-4}$  cm<sup>-1</sup>. The relative accuracy, i.e., the precision within the given band, of the peakfinder-evaluated lines is  $\pm 2 \times 10^{-4}$  cm<sup>-1</sup>.

# III. THEORY

# III.1. General

Due to the  $D_{3h}(M)$  symmetry three of the four fundamentals of trifluoroborane are infrared active:  $v_2(A_2'')$ ,  $v_3(E')$ , and  $v_4(E')$ . On the other hand, the  $v_1$  fundamental is only Raman active. Since the vibrational energy levels of the first excited states and of the upper state of the combination band  $v_1 + v_4$  are well separated from other levels, accidental resonances can be neglected.

However, the splitting of the rotational levels with K = 3 in the ground vibrational state as well as the splitting of the rotational levels with kl = -2 in the degenerate vibrational states  $v_3 = 1$ ,  $v_4 = 1$ , and  $v_1 = v_4 = 1$  have to be taken into account. As is well known, the splitting constants and their signs are observable quantities. Since nobody appears to have given explicitly a sign convention for the corresponding constants  $\Delta_3^0$  and  $t_i$ , this will be done below. It should, however, be noted that due to the spin statistics of BF<sub>3</sub> (Table II) all levels of rovibrational symmetry  $A'_1/A''_1$  have the statistical weight zero. Therefore, in the spectra of this molecule only a shift of the spin statistically allowed  $A'_2/A''_2$  levels may be observed.

All definitions and formulae in Sections III.2 and III.3 are given for the general case, i.e., for the case that both components of the doublet are allowed statistically. From these formulae the corresponding ones for  $BF_3$  may be deduced easily.

# III.2. Ground Vibrational State

The ground vibrational state energy is given up to fourth order by the well-known expression

_	<sup>10</sup> BF <sub>3</sub>	<sup>1 1</sup> BF <sub>3</sub>				
	$\Gamma_{s} = 28 A_{1} + 14 E$	$\Gamma_s = 16 A_1 + 8 E$				
	$\Gamma_{v_{RS}} = A_2$	$\Gamma_{vRS} = A_2$				
Γ <sub>ν R</sub>	ġ₅	Γ <sub>ν R</sub> g <sub>s</sub>				
A <sub>1</sub>	0	A <sub>1</sub> 0				
A2	28	A <sub>2</sub> 16				
E	14	E 8				

TABLE II

Spin Weights of the Rovibrational Levels for  ${}^{10}BF_3$  and  ${}^{11}BF_3$  (Group  $D_3(M)$ )

$$E(J, k) = B_0 J(J+1) + (C_0 - B_0) K^2 - D_J^0 J^2 (J+1)^2 - D_{JK}^0 J(J+1) K^2$$
  
-  $D_K^0 K^4 + H_{JJJ}^0 J^3 (J+1)^3 + H_{JJK}^0 J^2 (J+1)^2 K^2$   
+  $H_{JKK}^0 J(J+1) K^4 + H_{KKK}^0 K^6 + \delta_{3K} E(\hat{h}_{06}(s)), \quad (1)$ 

where  $\delta_{ij}$  is the Kronecker symbol.  $\hat{h}_{06}(s)$  denotes the splitting operator<sup>6</sup> giving rise to the splitting of all levels with K = 3 into an  $A''_1/A''_2$  doublet. All other symbols have their usual meanings.

As stated above, the sign convention of the corresponding splitting constant, as well as the correspondence of wave functions and energy levels, has to be defined clearly. This has been done for the familiar l-type doubling by Cartwright and Mills (15) and later on by Yamada (16). The definitions for the present case shall be derived in analogy to those given in Yamada's paper (16).

For  $D_{3h}(M)$  symmetry  $\hat{h}_{06}(s)$  is given in Ref. (17) as

$$\hat{h}_{06}(s) = \frac{1}{2} \Delta_3^0 \hbar^{-6} (\hat{J}_+^6 + \hat{J}_-^6), \qquad (2)$$

where  $\hat{J}_{\pm}$  represents  $\hat{J}_{\chi} \pm i \hat{J}_{\chi}$ . A suitable symmetrized basis is

$$|\pm\rangle = 2^{-1/2} [|J, k = +3\rangle \pm |J, k = -3\rangle].$$
 (3)

In order to determine the species of this basis with respect to the symmetry operations of  $D_{3h}(M)$  the operators  $R_z^{\beta}$  and  $R_{\alpha}^{\pi}$  originally introduced by Bunker (18) have to be used. Yamada (16) showed the operator  $R_{\alpha}^{\pi}$  acting on a symmetric-top wavefunction to change the phase factor of the latter by a factor  $\exp(2ik\rho)$ . Applying these two operators to our basis we may deduce the symmetry properties

$$(123)|\pm\rangle = |\pm\rangle \tag{4}$$

$$(23)|\pm\rangle = \pm (-1)^{J} [\cos(6\rho)|\pm\rangle - i\sin(6\rho)|\mp\rangle]$$
(5)

$$(E^*)|\pm\rangle = -|\pm\rangle. \tag{6}$$

According to Eqs. (4) and (6) all levels with K = 3 belong to  $A_1''$  or  $A_2''$ . As can be seen from Eq. (5), the behavior of the basis  $|\pm\rangle$  under the operation (23) depends on the rotational quantum number J and on the phase  $\rho$ . If we require these levels to be strictly symmetric or antisymmetric with respect to this latter operation,  $\rho$  has to be limited to the distinct values given by the equation

$$\rho = \frac{2n\pi}{6} \text{ (phase choice 1)} \quad \text{or} \quad \rho = \frac{(2n+1)\pi}{6} \text{ (phase choice 2)}$$
with  $n = 0, 1, 2, \cdots$  (7)

The phase choice 1, used in the present study, means that  $|+\rangle$  belongs to  $A_1''$   $(A_2'')$  for even (odd) J while the reverse is the case for  $|-\rangle$ .

The diagonal matrix element of  $\hat{h}_{06}(s)$  is the basis  $|\pm\rangle$  is also  $\rho$  dependent. Using Eq. (15) of Ref. (16) one obtains

298

<sup>&</sup>lt;sup>6</sup> Splitting operators are labelled by (s).

#### TABLE III

		(1)	Phase con g = 0	vention (2)	(see text) $g = -\frac{\pi}{6}$	Syı	nmetry
<b>∆</b> <sup>0</sup> <sub>3</sub>	level	<b>X</b> 9		<b>~</b> <sup>0</sup> <sub>3</sub>		Ţ	
·						even	odd
<b>&gt;</b> 0	upper	>0	+>	~0	->	<b>A</b> <sub>1</sub> "	A,"
20	lower	20	->	<b>L</b> O	+>	A2"	<b>A</b> 1
<0	upper	~0	l->	>0	+>	A2"	<b>A</b> 1
	lower		+>	>0	->	A1"	A2"

Correspondence between Energy Levels, Symmetry, and Wave Functions for K = 3 Levels of the Ground Vibrational State of a  $D_{3h}(M)$  Molecule

$$\langle \pm | \hat{h}_{06}(s) | \pm \rangle = \pm \exp(\pm 6i\rho) \frac{1}{2} \Delta_3^0 [J(J+1)] [J(J+1)-2] [J(J+1)-6].$$
 (8)

Here and in the following all operators  $\hat{h}_{mn}$  have been divided by hc. The limitations given by Eq. (7) are equivalent to the demand that the matrix elements of  $\hat{h}_{06}(s)$ , (8), always be real. Setting

$$\tilde{\Delta}_3^0 = \Delta_3^0 \exp(\pm 6i\rho),\tag{9}$$

we may rearrange Eq. (8) as

$$\langle \pm | \hat{h}_{06}(s) | \pm \rangle = \pm \frac{1}{2} \tilde{\Delta}_3^0 [J(J+1)] [J(J+1) - 2] [J(J+1) - 6].$$
 (10)

Combining Eqs. (4), (5), and (6) with Eq. (8), all possible cases of correspondence between energy levels, wave functions, and symmetry species may be obtained; these are listed in Table III. The important result is that for  $D_{3h}(M)$  molecules for positive  $\Delta_3^0$  the  $A_1''(A_2'')$  levels are above the  $A_2''(A_1'')$  levels for even (odd) J. For negative  $\Delta_3^0$  this relation is reversed.<sup>7</sup>

Until now  $\Delta_3^0$  has been evaluated only for a few small molecules, e.g., NH<sub>3</sub> (19, 20), ND<sub>3</sub> (21, 22), PH<sub>3</sub> (23–25), AsH<sub>3</sub> (26, 27), DCH<sub>3</sub> (28), DCF<sub>3</sub> (29), and <sup>10</sup>BF<sub>3</sub> (6.8), without explicit specification of phase choice and sign convention. This means that various authors use  $\tilde{\Delta}_3^0$  instead of  $\Delta_3^0$ . In some of the papers cited above the symmetry species of the split levels have been reported. Obviously, the sign convention adopted in Refs. (21, 24–27) agrees with that given in the present study, whereas the authors of the Refs. (20, 28, 29) have apparently used phase choice 2.

<sup>&</sup>lt;sup>7</sup> The sign convention for subgroups of  $D_{3h}(M)$  may be derived easily by using the correlation tables.

# III.3. Excited Vibrational States

The diagonal matrix elements for the excited vibrational states  $(v_2 = 1, l = 0)$ ,  $(v_3 = 1, l = \pm 1)$ ,  $(v_4 = 1, l = \pm 1)$ , and  $(v_1 = v_4 = 1, l = \pm 1)$  are given by

$$E(v, l, J, k) = v^{\circ} + B_{v}J(J+1) + (C_{v} - B_{v})K^{2} - D_{J}^{v}J^{2}(J+1)^{2}$$
  
$$- D_{JK}^{v}J(J+1)K^{2} - D_{K}^{v}K^{4} + H_{JJJ}^{v}J^{3}(J+1)^{3} + H_{JJK}^{v}J^{2}(J+1)^{2}K^{2}$$
  
$$+ H_{JKK}^{v}J(J+1)K^{4} + H_{KKK}^{v}K^{6} - kl[2(C\zeta)_{v} - \eta_{J}^{v}J(J+1)]$$
  
$$- \eta_{K}^{v}K^{2} - \eta_{JJ}^{v}J^{2}(J+1)^{2} - \eta_{JK}^{v}J(J+1)K^{2} - \eta_{KK}^{v}K^{4}] + E_{\text{split}}, \quad (11)$$

where all symbols have their usual meanings and  $E_{\text{split}}$  may be written using the Kronecker symbol  $\delta_{ij}$  as

$$E_{\text{split}} = \pm [\delta_{0l} \delta_{3k} \frac{1}{2} \Delta_{3}^{\nu} [J(J+1)] [J(J+1) - 2] [J(J+1) - 6]]$$
  
$$\mp [\delta_{\pm 1l} \delta_{\pm 1k} \frac{1}{2} q_{l} [J(J+1)]] + \delta_{\pm 1l} \delta_{\mp 2k} E(\hat{h}_{24}(s)). \quad (12)$$

The first term of Eq. (12) describes the splitting of the energy levels  $v_i = 1$ , K = 3 due to the operator  $\hat{h}_{06}(s)$ . Correspondingly, Eqs. (8)–(10) are valid if  $\Delta_3^0$  is exchanged for  $\Delta_3^v$ . Table III can also be used if the symmetry species of the functions  $|\pm\rangle$  are multiplied by the symmetry species of  $v_i$ . It was not possible to observe this splitting for  $v_2$  of <sup>10</sup>BF<sub>3</sub>. Consequently, it is not discussed further. The second term in Eq. (12) reproduces the well-known *l*-type doubling with the sign convention of Ref. (15).

The third term describes the splitting of the levels  $v_t = 1$ , kl = -2 which is caused by the operator  $\hat{h}_{24}(s)$ . This operator has to be invariant to Hermitian conjugation, time reversal, and the operations of the molecular symmetry group  $D_{3h}$ . Hence, a suitable form is

$$\hat{h}_{24}(s) = \hbar^{-4} f_{24}^{q} (q_{t+}^{2} \hat{J}_{+}^{4} + q_{t-}^{2} \hat{J}_{-}^{4}) + \hbar^{-6} f_{24}^{p} (p_{t+}^{2} \hat{J}_{+}^{4} + p_{t-}^{2} \hat{J}_{-}^{4}).$$
(13)

A proper and symmetry-adapted basis may be given by

$$|v_{t} = 1, \pm \rangle = 2^{-1/2} [|v_{t} = 1, l = +1, J, k = -2\rangle \\ \pm |v_{t} = 1, l = -1, J, k = +2\rangle].$$
(14)

Considering Eqs. (4), (5), and (6) in conjunction with Eq. (103) of Ref. (15), the symmetry properties of the basis  $|v_i = 1, \pm \rangle$  are obtained as

$$(123)|v_t = 1, \pm\rangle = |v_t = 1, \pm\rangle$$
(15)

$$(E^*) |v_t = 1, \pm\rangle = |v_t = 1, \pm\rangle$$
(16)

$$(23)|v_t=1,\pm\rangle=\pm(-1)^J[\cos(\delta+4\rho)|v_t=1,\pm\rangle$$

$$+ i \sin(\delta + 4\rho) | v_t = 1, \mp \rangle$$
], (17)

where  $\delta$  is defined by Eqs. (81) and (82) of Ref. (15). Equations (15)-(17) show that the basis  $|v_t = 1, \pm\rangle$  behaves symmetrically under (123) and (E\*), respectively, whereas its behavior with respect to (23) depends as well on the rotational quantum number J as on the phase ( $\delta + 4\rho$ ). This phase is by no means arbitrary. It may be determined in a unique way by the requirement that these basis functions belong either to  $A'_1$  or to  $A'_2$ . One obtains

$$(\delta + 4\rho) = 2n\pi$$
 (phase choice 1) or  
 $(\delta + 4\rho) = (2n+1)\pi$  (phase choice 2) with  $n = 0, 1, 2 \cdots$  (18)

In the present work phase choice 1 was applied, which classifies  $|v_t = 1, +\rangle$  as  $A'_1(A'_2)$  for even (odd) J, while the opposite is the case for  $|v_t = 1, -\rangle$ .

Using the ladder operators  $R^{+(+)}$  and  $R^{+(-)}$ , which are defined in Ref. (16), the diagonal matrix element of  $\hat{h}_{24}(s)$  may be obtained as

$$\langle v_t = 1, \pm | \hat{h}_{24}(s) | v_t = 1, \pm \rangle$$
  
=  $\pm \exp(\pm i[\delta + 4\rho]) \frac{1}{2} t_t [J(J+1)] [J(J+1) - 2], \quad (19)$ 

where  $t_t = 4(f_{24}^q + f_{24}^p)$ . It should be noted that the introduction of the phase choices given by Eq. (18) causes the diagonal matrix element of  $\hat{h}_{24}(s)$  in the basis (14) to become always real.

By defining

$$\tilde{t}_t = \exp(\pm i[\delta + 4\rho])t_t \tag{20}$$

Eq. (19) can be written as

$$\langle v_t = 1, \pm | \hat{h}_{24}(s) | v_t = 1, \pm \rangle = \pm \frac{1}{2} \tilde{t}_t [J(J+1)] [J(J+1) - 2].$$
 (21)

Using Eqs. (15)–(17) and (19) the correspondence between energy levels, wave functions, and symmetry species may be obtained (Table IV). Consequently, the sign convention of  $t_t$  in molecules of the molecular symmetry group  $D_{3h}$  is taken to be such that, for positive  $t_t$ , the splitting leads to the rovibrational  $A'_1(A'_2)$  levels lying

#### TABLE IV

Correspondence between Energy Levels, Symmetry, and Wave Functions for the  $v_i = 1$ , kl = -2 Levels of a  $D_{3h}(M)$  Molecule

Phase convention (1) (δ+4g)=0 (2					text) 4g)=n	Symmetry		
<u>t.</u>	level	Ĩ		Ĩ		Ţ		
						even	odd	
upper >0 lower	upper	>0	+>		l->	A'	A2	
	20	1->	<b>~</b> 0	+>	$\mathbf{A}_{2}^{\prime}$	A'		
	upper	.0	<b>↓</b> ->		+>	A <sub>2</sub>	A'	
<0 lower	lower	<0	+>	>0	->	<b>A</b> <sub>1</sub> '	Aź	

above the rovibrational  $A'_2(A'_1)$  levels for even (odd) J. For negative  $t_t$  the reverse is the case.<sup>8</sup>

Until now  $t_t$  constants have been evaluated only for a few small molecules or molecular ions, e.g., H<sub>3</sub>O<sup>+</sup> (30), NH<sub>3</sub> (31), AsH<sub>3</sub> (32), CH<sub>3</sub>D (33), CD<sub>3</sub>H (34, 35), PF<sub>3</sub> (36, 37), DCF<sub>3</sub> (29), OPF<sub>3</sub> (38), and <sup>11</sup>BF<sub>3</sub> (5). In all those papers the phase choice and the sign convention are not stated explicitly. Apparently, some of the authors have used  $\tilde{t}_t$  instead of  $t_t$ . Comparing the symmetry species of the split levels with the signs of  $t_t$ 's given makes it evident that all  $t_t$ 's in Refs. (32-35) are in fact  $\tilde{t}_t$ 's containing the phase factor ( $\delta + 4\rho$ ) =  $\pi$ . Only the authors of Ref. (29) appear to have adopted phase choice 1.

Since the  $r_t$  resonance is symmetry forbidden for  $D_{3h}(M)$  molecules (39), the only essential resonance which should be considered for <sup>10</sup>BF<sub>3</sub> is the  $q_t$  resonance expanded up to quartic order correction terms in J. The corresponding off-diagonal matrix element can be expressed by

$$\langle v_t = 1, l = 1, J, k+1 | h_{22} + h_{24} + h_{26} | v_t = 1, l = -1, J, k-1 \rangle$$

$$= -\frac{1}{2} (q_t + q_J J (J+1)) + (q_{JJ} J^2 (J+1)^2) [J (J+1) - k(k+1)]^{1/2} [J (J+1) - k(k-1)]^{1/2}.$$
(22)

Other types of resonances can be neglected for  ${}^{10}BF_3$  in the present study.

# IV. DESCRIPTION OF THE SPECTRA

# IV.1. The $v_2$ Fundamental and the Hot Band $2v_2 - v_2$

The fundamental  $\nu_2$  near 720 cm<sup>-1</sup>, which is a regular parallel band, exhibits medium intensity. The K structure of the P and R branches is well resolved for K > 6. The assignment of the  ${}^QR_K(J)$  and  ${}^QP_K(J)$  transitions was supported by previous studies (1, 7) as well as by the clearly discernible strong-weak-weak intensity alternation (Table II). 2629 rovibrational transitions could be assigned up to J = K = 75. A small part of the spectrum is shown in Fig. 1. In the Q branch the line density is so high (at about 2100 lines per cm<sup>-1</sup>) that no reasonable assignment can be given.  $\nu_2$  is accompanied by the hot bands  $\nu_2 + n\nu_4 - n\nu_4$  (n = 1, 2) and  $2\nu_2 - \nu_2$  (7). The latter has been reanalyzed during the course of this work. Altogether, 487 rovibrational transitions were assigned in the P and the R branches up to J = 40 and K = 21.

#### IV.2. The $v_3$ Fundamental

The very intense fundamental  $\nu_3$  is located at about 1500 cm<sup>-1</sup>. At a first glance its structure seems to be irregular. However, as Duncan (40) recognized, this "irregularity" is caused by a small negative subband spacing  $(C' - (C\zeta_3)' - B')$ . Thus, the  $K\Delta K > 0$  subband origins are red shifted in respect with the band center whereas the  $K\Delta K < 0$  subband origins are blue shifted.

<sup>&</sup>lt;sup>8</sup> This sign convention may be extended easily to the subgroups of  $D_{3h}(M)$  using the correlation tables.



FIG. 1. Detail of the  $\nu_2$  band of  ${}^{10}BF_3$ . (a) Experimental spectrum (resolution 0.0035 cm<sup>-1</sup>); some assignments are indicated, (b) Computed spectrum, hot bands omitted.



FIG. 2. A small portion of the  $\nu_3$  band of  ${}^{10}BF_3$ . (a) Experimental spectrum (resolution 0.0035 cm<sup>-1</sup>); some assignments are indicated. (b) Computed spectrum, hot bands omitted.

Starting from the results of Ref. (8), the assignment of 3882 rovibrational transitions could unambiguously be given up to J = 72 and K = 71. No hot band rovibrational transitions could be identified. A small portion of the spectrum is displayed in Fig. 2.

# IV.3. The $v_4$ Fundamental

The  $\nu_4$  fundamental is located at about 480 cm<sup>-1</sup>. Its intensity is comparable to that of  $\nu_2$ . At a first glance  $\nu_4$  reveals a parallel band structure with a prominent Q-branch region which is only about 5 cm<sup>-1</sup> wide. This structure originates in a very small subband spacing,  $(C' - (C\zeta_4)' - B')$ , which is about  $-3.4 \times 10^{-2}$  cm<sup>-1</sup>. Due to the high resolution available the peaks in the P and the R branches could be resolved up to a value of J = K = 70. Assignments were made using the parameters reported by Ginn *et al.* (3) and following the strong-weak-weak intensity alternation (Table II). In the Q branch a complete assignment is hampered by the high density of lines but many of them with K = 3 could certainly be identified. Two thousand six hundred ninety-one rovibrational transitions have been assigned, but no hot band lines were identified definitely. A small portion of the spectrum is shown in Fig. 3.

# IV.4. The Combination Band $v_1 + v_4$

The combination band  $v_1 + v_4$  lies at about 1360 cm<sup>-1</sup>. Due to its low intensity a sample pressure of 4 mbar had to be chosen which produces some pressure broadening and reduces the actual resolution (FWHM) to about 0.005 cm<sup>-1</sup>. The general structure of  $v_1 + v_4$  is very similar to that of  $v_4$ . With the knowledge of the molecular parameters of the latter band the analysis started with the assignment of the clearly discernible



FIG. 3. Detail of the  $\nu_4$  band of  ${}^{10}BF_3$ . (a) Experimental spectrum (resolution 0.0035 cm<sup>-1</sup>); some assignments are indicated. (b) Computed spectrum, hot bands omitted.



FIG. 4. A small part of the  $\nu_1 + \nu_4$  band of  ${}^{10}\text{BF}_3$ . (a) Experimental spectrum (resolution 0.0048 cm<sup>-1</sup>). (b) Computed spectrum, hot bands omitted.

peaks  ${}^{R}Q_{0}(J)$ ,  ${}^{R}R_{3n}(J)$ , and  ${}^{P}P_{3n}(J)$ , which were subjected to a least-squares fit (see below). The resulting first set of upper state constants allowed the prediction and identification of further lines. By repeating this procedure several times 2740 rovibrational transitions were assigned unambiguously up to J = K = 79. Small portions of the spectrum are reproduced in Figs. 4 and 5.



FIG. 5.  ${}^{R}Q_{0}(J)$  of the  $\nu_{1} + \nu_{4}$  band of  ${}^{10}\text{BF}_{3}$ ; some assignments are given. Because of the spin statistics for  $K'' \approx 0$  all rovibrational transitions with even J'' are forbidden. (a) Experimental spectrum (resolution 0.0048 cm<sup>-1</sup>). (b) Computed spectrum, hot bands omitted.

#### ZEISBERGER AND RUOFF

### V. DATA REDUCTION AND RESULTS

# V.1. Ground Vibrational State

As is well known, the parameters of the ground vibrational state can be obtained from the analysis of pure rotational transitions as well as by the method of combination differences of rovibrational transitions (IR-IR GSCD's). The huge data set obtained for  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ , and  $\nu_1 + \nu_4$  delivered 3139 IR-IR GSCD's up to J = 67 and K = 63. From these data  $B_0$ ,  $D_J^0$ ,  $D_{JK}^0$ ,  $H_{JJJ}^0$ ,  $H_{JJK}^0$ , and  $H_{JKK}^0$  can generally be derived, but not the parameters  $C_0$ ,  $D_K^0$ , and  $H_{KKK}^0$ . In the course of the fit routine, it became obvious that an additional consideration of  $\Delta_3^0$  improved the fit. On the other hand, the IR-IR GSCD's determine this  $\Delta_3^0$  constant only with low significance. Therefore, in first place it may only be considered as a pure correction term.

Recently, Yamamoto *et al.* (8) reported the observation of six pure rotational transitions in the ground vibrational state and 55 pure rotational transitions in the state  $v_3 = 1$  of <sup>10</sup>BF<sub>3</sub>. All those transitions are of the  $\Delta J = 0$  type with K between 3 and 8. Following Ref. (5), the combination of those rotational transitions in the state  $v_3 = 1$ with the IR transitions of  $v_3$  observed in the present study leads to 168 ground state combination differences (IR-MW-IR GSCD's) of the types  ${}^NO_K(J)$ ,  ${}^NP_K(J)$ ,  ${}^NQ_K(J)$ ,  ${}^NR_K(J)$ , and  ${}^NS_K(J)$ . As an example, the construction of  ${}^NO_6$  (12) is illustrated in Fig. 6. Since the very precisely measured ground state rotational transitions belong to K'' = 3 as well as most of the IR-MW-IR GSCD's do, it can be stated that these transitions depend mainly on  $C_0$  and  $\Delta_3^0$  and to a lesser extent on  $D_K^0$  and  $H_{KKK}^0$ .

Consequently, the ground state constants were adjusted in two steps. In the first one  $B_0$ ,  $D_J^0$ ,  $D_{JK}^0$ ,  $H_{JJJ}^0$ ,  $H_{JJK}^0$ ,  $H_{JKK}^0$ , and a rough value of  $\Delta_3^0$  were obtained from the IR-IR GSCD's according to Eqs. (1) and (10). The result labelled by (b) is listed in Table V, reproducing the data with  $\sigma = 3.8 \times 10^{-4}$  cm<sup>-1</sup>, which agrees with the experimental accuracy. The low significance of  $\Delta_3^0$ (b) is evident.



FIG. 6. Schematic diagram of the construction of the IR-MW-IR GSCD  ${}^{N}O_{6}(12)$  from the rovibrational transitions  ${}^{R}R_{3}(10)$  and  ${}^{P}P_{6}(12)$  of  $v_{3}$  and from the pure rotational transition  ${}^{R}Q_{4}(11)$  in the state  $v_{3} = 1$ .

TA	BL	Æ	٧
		_	

Ground State Constants of  ${}^{10}BF_3$  (cm<sup>-1</sup>) (a)

<u> </u>	This work	Ref. ( <u>7</u> ),( <u>8</u> )
B <sub>0</sub>	0.34499628(23) (b)	0.345008(2) (f)
DJ	4.3021(15)x10 <sup>-7</sup> (b)	4.338(11)x10 <sup>-7</sup> (f)
D <sup>0</sup> <sub>J K</sub>	-7.5876(33)x10 <sup>-7</sup> (b)	$-7.530(30) \times 10^{-7}$ (f)
D <sub>K</sub>	3.5396x10 <sup>-7</sup> (e)	3.526(14)x10 <sup>-7</sup> (f)
H <sup>0</sup> JJJ	$1.313(30) \times 10^{-12}$ (b)	-
Н <sup>0</sup> ЈЈК	$-5.040(99) \times 10^{-12}$ (b)	-
Н <sup>0</sup> кк	6.27(14)x10 <sup>-12</sup> (b)	-
Н <sup>0</sup> к к	-2.523x10 <sup>-12</sup> (e)	-
<b>∆</b> <sup>0</sup> <sub>3</sub>	$-1.70(31) \times 10^{-13}$ (b)	-1.7910(70)x10 <sup>-13</sup> (f,g)
σ(b,d)	0.00038	-
Co	0.17215192(10) (c)	0.17216583(8) (f)
$\Delta_3^0$	-1.5319(84)x10 <sup>-13</sup> (c)	-
<b>6</b> (c,d)	0.00035	-
o(f,d)	-	0.00089

(a) the numbers in parentheses represent one standard deviation in units of the last digit
(b) from IR-IR GSCD, see text
(c) from IR-MW-IR GSCD, see text
(d) standard deviation of the fit
(e) from planarity conditions (<u>17</u>), held fixed
(f) global fit

(g) sign convention not defined

In the second step, we tried to fit  $C_0$ ,  $D_K^0$ ,  $H_{KKK}^0$ , and  $\Delta_3^0$  on the basis of the 168 IR-MW-IR GSCD's and six ground state rotational transitions. Because of the different accuracies the pure rotational transitions have been weighted more than the IR-MW-IR GSCD's by a factor of 10<sup>5</sup> in the least-squares fit. All other constants except  $\Delta_3^0$  were fixed to the values determined in the first step. During the fit it became obvious that only  $C_0$  and  $\Delta_3^0$  were significantly adjustable. The result labelled by (c) is also listed in Table V; the corresponding standard deviation was  $\sigma = 3.5 \times 10^{-4}$  cm<sup>-1</sup>.  $D_K^0$  and  $H_{KKK}^0$  were constrained to the values given by the planarity conditions (17). A comparison with previous results (7, 8) shows that the present spectroscopic constants are more accurate, except  $C_0$  and  $\Delta_3^0$ . In the present study the sextic centrifugal distortion constants were determined for the first time.

# V.2. Excited Vibrational States

The modified iterative program MILLI (41), which held the ground vibrational state constants fixed during the fit, was applied to refine the upper vibrational state

parameters and interaction constants. For the excited states, except  $v_2 = 2$ , two different approximations were chosen according to Eq. (11). In the first one (Model I) the contributions were considered up to fourth order whereas the second one (Model II) includes additionally  $\hat{h}_{25}$  and  $\hat{h}_{26}$ . Due to the resolution available, the shift of all transitions with K'' = 3, which is caused by the splitting operators, could be detected only in the case of the perpendicular bands  $v_3$ ,  $v_4$ , and  $v_1 + v_4$ . Considering Eqs. (10) and (21) and taking into account the chosen sign conventions and the spin weights (Table II), the shifted transitions  ${}^{P}P_3(J)_s$ ,  ${}^{P}Q_3(J)_s$ , and  ${}^{P}R_3(J)_s$  may be obtained as

$${}^{P}P_{3}(J)_{s} = {}^{P}P_{3}(J) \pm [\sigma_{t}T'_{(J-1)} + \sigma_{u}U''_{J}]$$

$${}^{P}R_{3}(J)_{s} = {}^{P}R_{3}(J) \pm [\sigma_{t}T'_{(J+1)} + \sigma_{u}U''_{J}]$$

$${}^{P}Q_{3}(J)_{s} = {}^{P}Q_{3}(J) \mp [\sigma_{t}T'_{J} - \sigma_{u}U''_{J}],$$
(23)

where  ${}^{P}P_{3}(J)$ ,  ${}^{P}Q_{3}(J)$ , and  ${}^{P}R_{3}(J)$  represent the unshifted lines. The upper (lower) sign correlates to even (odd) J. The other symbols may be expressed as

$$\sigma_t = \text{sign of } t_t$$
  

$$\sigma_u = \text{sign of } \Delta_3^0$$
  

$$T_a = \frac{1}{2} |t_t| [a(a+1)] [a(a+1) - 2]$$
  

$$U_a = \frac{1}{2} |\Delta_3^0| [a(a+1)] [a(a+1) - 2] [a(a+1) - 6].$$



FIG. 7. Schematic energy diagram of the shifted rovibrational transitions  ${}^{P}R_{3}(J)_{s}$ ,  ${}^{P}Q_{3}(J)_{s}$ , and  ${}^{P}P_{3}(J)_{s}$ , for  $\Delta_{0}^{0} > 0$ ,  $t_{t} > 0$ , and even J (see text). Note that the dipole moment operator along a space fixed axis belongs to the species  $A_{1}^{"}$  of  $D_{3h}(M)$ . (Unshifted levels are indicated by broken lines.)

In Fig. 7 the shifted transitions have been drawn schematically for  $\Delta_3^0 > 0$ ,  $t_t > 0$ , and even J. The constant  $t_t$  was adjusted in a least-squares fit, using Eq. (23) and fixing  $\Delta_3^0$  to the value  $\Delta_3^0(c)$  of Table V.

In order to confirm the assignment, the adjusted excited state parameters were used as input for the program KILO (41) which simulates rovibrational spectra of symmetric top molecules.

V.2.1. The upper state  $v_2 = 1$ . The upper state constants of  $v_2$  in Table VI were obtained by a fit of 2629 rovibrational transitions. The standard deviation was  $\sigma = 2.4$  $\times 10^{-4}$  cm<sup>-1</sup> for Model I and  $2.3 \times 10^{-4}$  cm<sup>-1</sup> for Model II, respectively. Thus, both models reproduce the data comparably well. However, some constants, e.g.,  $D''_{IK} - D'_{IK}$ , differ significantly. All constants except the last agree well with those reported by Yamamoto et al. (7). In the present work, however, the precision is improved considerably. Apparently, the constant  $D'_{IK} - D'_{IK}$  is poorly adjustable in all cases.

V.2.2. The upper state  $v_2 = 2$ . Fixing the lower state constants of the hot band  $2\nu_2 - \nu_2$  to those obtained for  $\nu_2$ , the analysis of the 487 observed transitions leads only to the band origin, B'' - B', C'' - C',  $D''_J - D'_J$ , and  $D''_{JK} - D'_{JK}$  (Table VII). As expected, B'' - B' and C'' - C' resemble the corresponding values of  $\nu_2$ , which is not the case for  $D''_J - D'_J$  and  $D''_{JK} - D'_{JK}$ , respectively. Obviously, these latter constants are not well defined. This is also reflected by a relatively high standard deviation of these constants in the fit of Yamamoto et al. (7). All molecular parameters given in Ref. (7), which are significantly determined, agree well with the present results.

The anharmonicity constant  $x_{22}$  could be obtained as 1.334 cm<sup>-1</sup> from the band origins of  $\nu_2$  and  $2\nu_2 - \nu_2$ . This result is of the same order of magnitude as a value of

Molecular Constants for $\nu_2$ of ${}^{10}\text{BF}_3$ (cm <sup>-1</sup> ) (a)							
	This work Model I	Model II	Ref. ( <u>7</u> )				
ν <sup>o</sup> 2	719.285004(16)	719.285054(22)	719.28540(12)				
B"-B'	-1.13589(18)x10-4	-1.13341(43)x10 <sup>-4</sup>	-1.14(4)x10 <sup>-4</sup>				
c"-c′	-2.85879(21)x10-4	-2.85966(51)x10-4	-2.854(4)x10-4				
$D_J^{"} - D_J^{'}$	-1.0655(48)x10-9	-8.99(23)x10 <sup>-10</sup>	-1.5(24)x10 <sup>-9</sup>				
D" K - D' K	-4.3(11)x10 <sup>-11</sup>	-3.56(49)x10 <sup>-10</sup>	1.0(60)x10-9				
D <sub>κ</sub> " - D <sub>κ</sub>	7.548(87)x10 <sup>-10</sup>	8.27(40)x10 <sup>-10</sup>	8(5)x10 <sup>-10</sup>				
H <sub>JJJ</sub> ~H <sub>JJJ</sub>	-	2.87(36)x10 <sup>-14</sup>	-				
$\mathbf{H}_{\mathbf{J}\mathbf{J}\mathbf{K}}^{*} - \mathbf{H}_{\mathbf{J}\mathbf{J}\mathbf{K}}^{\prime}$	-	-8.5(11)x10 <sup>-14</sup>	-				
H <sub>J K K</sub> -H <sub>J K K</sub>	-	9.3(16)x10 <sup>-14</sup>	-				
$H_{K K K}^{"} - H_{K K K}^{\prime}$	-	-5.52(98)x10 <sup>-14</sup>	-				
б(Ъ)	0.00024	0.00023	0.00089				

TABLE VI

(a) numbers in parentheses represent one standard deviation in units of the last digit(b) standard deviation of the fit

TABLE VII
Molecular Constants for $2\nu_2 - \nu_2$ of <sup>10</sup> BF <sub>3</sub> (cm <sup>-1</sup> ) (a)

	This work	Ref. ( <u>7</u> )
$(2v_2 - v_2)^0$	721.95351(7)	721.9533(6)
B"-B'	-9.090(19)x10 <sup>-5</sup>	-9.5(2)x10 <sup>-5</sup>
C"-C'	-2.8104(37)x10 <sup>-4</sup>	-2.80(3)x10 <sup>-4</sup>
D," -D,	1.8(12)x10 <sup>-10</sup>	-4.1(13)x10-9
D <sub>J к</sub> -D <sub>J к</sub>	-5.70(39)x10 <sup>-9</sup>	3.0(30)x10 <sup>-9</sup>
$D_{\kappa}^{"} - D_{\kappa}^{\prime}$	0 (c)	6(6)x10 <sup>-9</sup>
б(Ъ)	0.00040	0.00107
x <sub>2 2</sub>	1.334	1.334

(a) numbers in parentheses represent one standard deviation in units of the last digit(b) standard deviation of the fit

(c) fixed

 $2.27 \text{ cm}^{-1}$  calculated by Ginn *et al.* (42) by assuming an anharmonic potential function for BF<sub>3</sub>.

V.2.3. The upper state  $v_3 = 1$ . The spectroscopic constants for the  $v_3 = 1$  state derived from 3882 assigned rovibration transitions are collected together in Table VIII. Here the standard deviation of the fit is  $\sigma = 3.5 \times 10^{-4}$  cm<sup>-1</sup> for Model I and  $\sigma = 2.9 \times 10^{-4}$  cm<sup>-1</sup> for Model II, respectively. Since the constants  $H''_{JJK} - H'_{JJK}$  and  $H''_{KKK} - H'_{KKK}$  could not be obtained satisfactorily in Model II, they were constrained to typical values during the fit.

The lower-order constants of both models are in good agreement whereas the higherorder ones differ significantly. The present results also agree reasonably well with the parameters reported by Yamamoto et al. (8). With the exception of  $q_3$  all constants presented in this paper are more precise than those of Ref. (8).

V.2.4. The upper state  $v_4 = 1$ . The parameters for  $v_4 = 1$  were determined by fitting 2691 rovibrational transitions and are listed in Table IX. Model I and Model II reproduce these data with the standard deviations  $\sigma = 3.2 \times 10^{-4}$  cm<sup>-1</sup> and  $\sigma = 2.9$  $\times 10^{-4}$  cm<sup>-1</sup>, respectively. Some higher-order constants in Model I are not in accordance with the corresponding ones in Model II. The present values are much more precise than those of previous studies (3, 7).

V.2.5. The upper states  $v_1 = v_4 = 1$  and  $v_1 = 1$ . Table X presents the resulting parameters for the state  $v_1 = v_4 = 1$ , which has never been studied before with high resolution. The standard deviation of the least-squares analysis of 2740 rovibrational transitions was  $\sigma = 4.8 \times 10^{-4}$  cm<sup>-1</sup> in Model I and  $\sigma = 3.4 \times 10^{-4}$  cm<sup>-1</sup> in Model II, respectively. As in the fits of the other bands studied in the present investigation, the higher-order constants in both models exhibit differences which by far exceed the added standard deviations.

Combining these results with those of  $v_4$  some constants of the state  $v_1 = 1$  may be deduced which are given in Table XI. The vibrational Raman spectrum of gaseous

#### TABLE VIII

Molecular Constants for  $\nu_3$  of  ${}^{10}BF_3$  (cm<sup>-1</sup>) (a)

	This Model I	work Model II	Ref. ( <u>8</u> )		
ν <sup>0</sup> <sub>3</sub>	1505.780448(14)	1505.780268(16)	1505.77923(12)		
B"-B'	1.521398(24)x10-	<sup>3</sup> 1.520757(38)x10 <sup>-3</sup>	<sup>3</sup> 1.5206(25)x10 <sup>-3</sup>		
C"-C′	8.39347(26)x10 <sup>-4</sup>	8.38993(46)x10 <sup>-4</sup>	8.3933(78)x10 <sup>-4</sup>		
(Cζ <sub>3</sub> )'	0.13449831(29)	0.13449530(44)	0.1344937(60)		
$D_{J}^{"} - D_{J}^{\prime}$	6.466(90)x10 <sup>-10</sup>	1.46(23)x10 <sup>-10</sup>	-2.0(50)x10 <sup>-10</sup>		
D" K -D' K	-7.48(24)x10 <sup>-10</sup>	-8.4(23)x10 <sup>-11</sup>	-1.0(12)x10 <sup>-10</sup>		
D"-D'	8.66(17)x10 <sup>-10</sup>	4.48(28)x10 <sup>-10</sup>	6.0(20)x10 <sup>-10</sup>		
η <sub>σ</sub>	5.0548(39)x10 <sup>-7</sup>	5.168(11)x10 <sup>-7</sup>	5.065(12)x10 <sup>-7</sup>		
η <sub>κ</sub>	-3.1785(42)x10 <sup>-7</sup>	-3.471(12)x10 <sup>-7</sup>	-3.33(5)x10 <sup>-7</sup>		
H <sub>J J J</sub> -H <sub>J J J</sub>	-	-1.002(36)x10 <sup>-13</sup>	-		
Н <sub>ЈЈК</sub> -Н <sub>ЈЈК</sub>	-	2.193x10 <sup>-13</sup> (c)	-		
Н <sub>Ј к к</sub> ~Н <sub>Ј к к</sub>	-	-2.366(63)x10 <sup>-13</sup>	-		
H <sub>κ κ κ</sub> -Η <sub>κ κ κ</sub>	-	7.760x10 <sup>-14</sup> (c)	-		
η <sub>σσ</sub>	-	-8.27(36)x10 <sup>-12</sup>	-		
η <sub>υ κ</sub>	-	2.492(76)x10 <sup>-11</sup>	-		
η <sub>κ κ</sub>	-	-1.320(47)x10 <sup>-11</sup>	-		
$q_3$	1.8141(24)x10 <sup>-4</sup>	1.8363(38)x10-4	1.8330(18)x10 <sup>-4</sup>		
ď	-6.57(14)x10 <sup>-9</sup>	-8.96(46)x10-9	-8.16(18)x10 <sup>-9</sup>		
ď <sup>a a</sup>	-	5.3(12)x10 <sup>-13</sup>	-		
t <sub>3</sub>	7.410(44)x10 <sup>-9</sup>	7.423(42)x10 <sup>-9</sup>	-6.7x10 <sup>-9</sup> (d)		
<b>G</b> (b)	0.00035	0.00029	0.00070		
<ul> <li>(a) numbers in parentheses represent one standard deviation in units of the last digit</li> <li>(b) standard deviation of the fit</li> <li>(c) fixed to typical values</li> <li>(d) fixed to the value of <sup>11</sup>BF<sub>2</sub>: sign convention not defined</li> </ul>					

BF<sub>3</sub> was recorded in the thirties (44, 45); since that time no reexamination is known. Therefore, it is not surprising that the only information known on  $v_1$  is the so-called "Raman frequency" which is reported to be 886 cm<sup>-1</sup> (44) and 888 cm<sup>-1</sup> (45). This agrees quite well with the present results: referring to a calculated value of -6.43 cm<sup>-1</sup> for  $x_{14}$  (42),  $v_1^0$  is obtained as approximately 889 cm<sup>-1</sup>. Anyway, a high resolution Raman study of  $v_1$  would be highly desirable. Another constant which can be derived from the present results is the vibrational contribution from the state  $v_1 = 1$  to ( $C\zeta_4$ ),

#### TABLE IX

Molecular	Constants	for	v. of	<sup>10</sup> BF <sub>2</sub>	(cm <sup>-1</sup>	) (	้ล่	)
, totocului	Combianto	101	P4 01		( 0111		ч.	,

	This work		Ref. ( <u>3</u> )	Ref. ( <u>7</u> ) (d)
	Model I	Model II		
v04	481.128612(16)	481.128666(19)	481.238(3)	-
B*-B'	-5.04642(34)x10 <sup>-4</sup>	-5.04028(73)x10 <sup>-4</sup>	-4.9(2)x10 <sup>-4</sup>	-4.96(5)x10-4
C*-C'	9.5576(34)x10 <sup>-5</sup>	9.53155(72)x10 <sup>-5</sup>	-	(e)
(c; <sub>4</sub> )′	-0.13960791(39)	-0.13960579(66)	(c)	(c)
D <sub>j</sub> "-D <sub>j</sub>	-1.934(15)x10 <sup>-9</sup>	-1.142(71)x10 <sup>-9</sup>	3(3)x10 <sup>-8</sup>	8.8(20)x10 <sup>-9</sup>
D <sub>JK</sub> - D <sub>JK</sub>	6.410(34)×10 <sup>-9</sup>	4.37(16)x10 <sup>-9</sup>	2(6)x10 <sup>-8</sup>	-2(5)x10 <sup>-9</sup>
D_K - D_K	-4.452(24)×10 <sup>-9</sup>	-3.38(10)x10	1(6)x10 <sup>-8</sup>	-
η <sub>J</sub>	-1.51318(63)x10 <sup>-6</sup>	-1.5139(24)x10 <sup>-6</sup>	-	-1.65(6)x10 <sup>-6</sup>
יי <sub>א</sub>	1.45484(70)×10-6	1. <b>464</b> 3(26)x10 <sup>-6</sup>	-	-
н <sub>јјј</sub> -н <sub>јјј</sub>	- :	2.36(18)x10 <sup>-13</sup>	-	-
н <sub>јјк</sub> −н <sub>јјк</sub>	-	-9.03(57)x10 <sup>-13</sup>	-	-
H <sub>JKK</sub> -H <sub>JKK</sub>	-	1.002(67)x10 <sup>-12</sup>	-	-
H <sub>KKK</sub> -H <sub>KKK</sub>	-	-3.82(33)x10-13	-	-
ח <sub>3 3</sub>	-	3.05(96)x10 <sup>-12</sup>	-	-
η <sub>JK</sub>	-	-9.8(18)x10 <sup>-12</sup>	-	-
η <sub>κ κ</sub>	-	4.2(12)x10 <sup>-12</sup>	-	-
<b>q</b> 4	6.99728(82)x10 <sup>-4</sup>	7.0221(16)x10-4	-	6.94(4)×10 <sup>-4</sup>
ď	-3.240(39)×10 <sup>-9</sup>	-6.32(19)x10 <sup>-9</sup>	-	-
d <sup>2 2</sup>	-	8.42(50)x10 <sup>-13</sup>	-	-
t <sub>4</sub>	4.34(56)×10 <sup>-10</sup>	4.67(46)x10 <sup>-10</sup>	-	-
б (Ъ)	0.00032	0.00029	0.01	0.00074
η <sub>41</sub>	2.654×10 <sup>-3</sup> (f)	2.657x10 <sup>-3</sup>		-

(a) numbers in parentheses represent one standard deviation in units of the last digit

```
(b) standard deviation of the fit
```

```
(b) Standard deviation of the fit
(c) \zeta_4 = 0.809 (dimensionless)
(d) from v_2 + v_4 - v_4
(e) C' was estimated to be 0.172049 cm<sup>-1</sup> on the basis of B<sub>0</sub> and the inertial
```

```
defect (<u>43</u>)
```

(f) see text

 $\eta_{14}$  (46). Using the third-order approximation of Ref. (46), the value of this latter constant was found to be  $2.654 \times 10^{-3}$  cm<sup>-1</sup>. It should be noted that within the added standard deviations  $t_4$  and  $t_{14}$  are in good agreement.

IABLE 2
---------

Molecular Constants for  $v_1 + v_4$  of <sup>10</sup>BF<sub>3</sub> (cm<sup>-1</sup>) (a)

	This work Model I	Model II
$(v_1 + v_4)^0$	1363.658466(22)	1363.658828(20)
B"-B'	1.82709(48)x10-4	1.84103(78)x10 <sup>-4</sup>
C"-C'	4.60829(29)x10 <sup>-4</sup>	4.61291(45)x10 <sup>-4</sup>
(C <b>Ç<sub>14</sub>)</b> ′	-0.13695431(47)	-0.13694857(62)
$D_{J}^{"} - D_{J}^{\prime}$	-3.340(23)x10 <sup>-9</sup>	~2.296(84)x10 <sup>-9</sup>
D <sub>J K</sub> -D <sub>J K</sub>	8.262(49)x10 <sup>-9</sup>	6.30(16)x10 <sup>-9</sup>
$D_{\kappa}^{*} - D_{\kappa}^{\prime}$	-5.649(28)x10 <sup>-9</sup>	-4.544(86)x10 <sup>-9</sup>
$\eta_J$	-1.58352(84)x10 <sup>-6</sup>	-1.5834(25)x10 <sup>-6</sup>
η <sub>κ</sub>	1.39660(82)x10 <sup>-6</sup>	1.4117(24)x10 <sup>-6</sup>
H <sub>3</sub> ", , ~H <sub>3</sub> ", ,	-	1.68(25)x10 <sup>-13</sup>
$H_{JJK}^{"} - H_{JJK}^{\prime}$	-	-5.23(69)x10 <sup>-13</sup>
$H_{JKK}'' = H_{JKK}'$	-	5.09(69)x10 <sup>-13</sup>
H" - H' K K	-	-1.39(26))x10 <sup>-13</sup>
η <sub>υ υ</sub>	-	1.8(12)x10 <sup>-12</sup>
η <sub>JK</sub>	-	-1.04(21)x10 <sup>-11</sup>
η <sub>κ κ</sub>	-	5.9(11)x10 <sup>-12</sup>
<b>q</b> <sub>1 4</sub>	7.3755(12)x10 <sup>-4</sup>	7.4101(18)x10-4
$\mathbf{d}^{2}$	-3.369(62)x10 <sup>-9</sup>	-6.50(10)x10 <sup>-9</sup>
d <sup>1 1</sup>	-	5.23(60)x10 <sup>-13</sup>
t <sub>14</sub>	5.72(71)x10 <sup>-10</sup>	6.54(59)x10 <sup>-10</sup>
σ(b)	0.00048	0.00034

(a) numbers in parentheses represent one standard deviation in units of the last digit

(b) standard deviation of the fit

V.2.6. Equilibrium structure. In the present study, precise rotational constants for the ground vibrational state as well as for all four fundamentals of  ${}^{10}\text{BF}_3$  have been obtained.

The well-known relation

$$X_0 - X' = \sum_i \alpha_i^X, \qquad (24)$$

in which X denotes B or C, is valid up to fourth order, where the  $\alpha$ 's represent the diagonal elements of  $\hat{h}_{22}$ . The next higher contribution to Eq. (24) originates in the corresponding elements of  $\hat{h}_{42}$ , i.e., in the  $\gamma_{ij}^{x}$ 's. Ignoring these latter and all higher-

INDLL M	TA	BL	Æ	XI
---------	----	----	---	----

Estimated Molecular Constants for  $\nu_1$  of <sup>10</sup>BF<sub>3</sub> (cm<sup>-1</sup>) (a)

v <sup>0</sup> + X <sub>14</sub>	882.530
B"-B'	6.874x10 <sup>-4</sup>
C"-C'	3.653x10-4
$D_{J}$ " – $D_{J}$	-1.4×10 <sup>-9</sup>
D <sub>J K</sub> -D <sub>J K</sub>	1.9x10 <sup>-9</sup>
$D_{\kappa}^{"} = D_{\kappa}^{\prime}$	-1.2x10 <sup>-9</sup>

order parameters, the error in Eq. (24) may be estimated conservatively to be not more than 2%. Hence, for  ${}^{10}BF_3$ , the resulting equilibrium rotational constants are

$$B_e = 0.34630(3) \text{ cm}^{-1}$$

$$C_e = 0.17313(2) \text{ cm}^{-1}.$$
(25)

Within the sum of both errors, these constants satisfy the planarity condition (17)

$$B_e = 2C_e. \tag{26}$$

Thus, the present  $B_e$  agrees well with that of 0.34628(5) cm<sup>-1</sup> reported by Yamamoto *et al.* (7).

From the constants given in Eq. (25) the equilibrium internuclear boron-fluorine distance<sup>9</sup>  $r_e$  is deduced to be 1.3070(1) Å, which is in perfect agreement with the previous result of Ref. (7).

## VI. CONCLUSION

In the present study the high-resolution Fourier transform infrared spectrum of  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_1 + \nu_4$ , and  $2\nu_2 - \nu_2$  of isotopically enriched <sup>10</sup>BF<sub>3</sub> has been investigated. A total of about 12 500 vibration-rotation transitions have been measured and assigned. After a careful definition of the sign convention of the splitting constants  $\Delta_3^0$  and  $t_i$ , ground state constants and parameters for the excited states have been considerably improved. From these data a set of constants for the Raman active  $\nu_1$  has been established which will be helpful for future Raman investigations. The standard deviations of all fits agree quite well within the experimental accuracy. This indicates that the analyzed bands are not perturbed by accidental resonances.

The analysis of the corresponding spectra of isotopically enriched  ${}^{11}\text{BF}_3$  is under progress and will be reported elsewhere (11).

#### ACKNOWLEDGMENTS

The authors thank Dipl. Ing. K. Lattner, Dipl. Phys. J. Gast, Dr. L. Wunsch, and Miss E. Kaltenecker for technical assistance. One of us (E.Z.) expresses his gratitude to the Physikalisch-Chemisches Institut der

## FTIR SPECTRA OF <sup>10</sup>BF<sub>3</sub> 315

Justus-Liebig-Universität, Giessen, for the hospitality extended to him during his work in Giessen and to the Ministerium für Wissenschaft und Kunst Baden-Württemberg for a fellowship.

The experimental work was supported by funds of the Universität Ulm, the Deutsche Forschungsgemeinschaft, and the Fonds der chemischen Industrie. All calculations were carried out at the Bereichsrechenzentrum der Universität Ulm, a service that is gratefully acknowledged. The programs MILLI and KILO were made available to us through the courtesy of Dr. G. Graner of the Universit de Paris-Sud, Orsay, France.

We also express our thanks to Dr. J. Vogt for critically reading and commenting on the manuscript and to Miss E. Ruoff for bringing some stylistic errors to our attention.

#### **RECEIVED: January 3, 1989**

#### REFERENCES

- I. S. G. W. GINN, J. K. KENNEY, AND J. OVEREND, J. Chem. Phys. 48, 1571-1579 (1968).
- 2. S.G.W. GINN, C.W. BROWN, J.K. KENNEY, AND J. OVEREND, J. Mol. Spectrosc. 28, 509-525 (1968).
- 3. S. G. W. GINN, D. JOHANSEN, AND J. OVEREND, J. Mol. Spectrosc. 36, 448-463 (1970).
- 4. P. A. FREEDMAN AND W. J. JONES, J. Mol. Spectrosc. 54, 182–190 (1975).
- 5. S. YAMAMOTO, K. KUCHITSU, T. NAKANAGA, H. TAKEO, C. MATSUMURA, AND M. TAKAMI, J. Chem. Phys. 83, 1444–1448 (1985).
- 6. S. YAMAMOTO, T. NAKANAGA, H. TAKEO, C. MATSUMURA, M. TAKAMI, AND K. KUCHITSU, *Chem. Phys. Lett.* **122**, 9–11 (1985).
- 7. S. YAMAMOTO, R. KUWABARA, M. TAKAMI, AND K. KUCHITSU, J. Mol. Spectrosc. 115, 333-352 (1986).
- 8. S. YAMAMOTO, K. KUCHITSU, T. NAKANAGA, H. TAKEO, C. MATSUMURA, AND M. TAKAMI, J. Chem. Phys. 84, 6027–6033 (1986).
- 9. M. OLDANI AND A. BAUDER, J. Chem. Phys. 86, 624-628 (1987).
- G. M. PLUMMER, G. WINNEWISSER, M. WINNEWISSER, J. HAHN, AND K. REINARTZ, J. Mol. Spectrosc. 126, 255-269 (1987).
- 11. E. ZEISBERGER AND A. RUOFF, manuscript in preparation.
- 12. A. ENGELBRECHT, Angew. Chem. Intern. Ed. Engl. 4, 641-651 (1968).
- 13. G. GUELACHVILI AND K. NARAHARI RAO, "Handbook of Infrared Standards," Academic Press, New York, 1986.
- 14. L. R. BROWN AND R. A. TOTH, J. Opt. Soc. Amer. B 2, 842-856 (1985).
- 15. G. J. CARTWRIGHT AND I. M. MILLS, J. Mol. Spectrosc. 34, 415-439 (1970).
- 16. K. YAMADA, Z. Naturforsch. A 38, 821-834 (1983).
- J. K. G. WATSON, in "Vibrational Spectra and Structure," Vol. 6, pp. 2–89, Elsevier, Amsterdam/New York, 1977.
- 18. P. R. BUNKER, "Molecular Symmetry and Spectroscopy," Academic Press, New York, 1979.
- 19. Š. URBAN, D. PAPOUŠEK, J. KAUPPINEN, K. YAMADA, AND G. WINNEWISSER, J. Mol. Spectrosc. 101, 1-15 (1983).
- 20. Y. UEDA AND J. IWAHORI, J. Mol. Spectrosc. 116, 191-213 (1986).
- 21. V. MALATHY DEVI, P. P. DAS, K. NARAHARI RAO, Š. URBAN, D. PAPOUŠEK, AND V. SPIRKO, J. Mol. Spectrosc. 88, 293–299 (1981).
- 22. S. URBAN, D. PAPOUŠEK, M. BESTER, K. YAMADA, G. WINNEWISSER, AND A. GUARNIERI, J. Mol. Spectrosc. 106, 29–37 (1984).
- 23. P. BERNARD AND T. OKA, J. Mol. Spectrosc. 75, 181-196 (1979).
- 24. G. TARRAGO AND M. DANG-NHU, J. Mol. Spectrosc. 111, 425-439 (1985).
- 25. Y. CHEN, J. M. FRYE, AND T. OKA, J. Opt. Soc. Amer. B 3, 935-939 (1986).
- 26. W. M. B. OLSON, A. G. MAKI, AND R. L. SAMS, J. Mol. Spectrosc. 55, 252-270 (1975).
- 27. M. CARLOTTI, G. DI LONARDO, AND L. FUSINA, J. Mol. Spectrosc. 102, 310-319 (1983).
- 28. C. CHAKERIAN, JR., AND G. GUELACHVILI, J. Mol. Spectrosc. 84, 447-456 (1980).
- 29. J. SAKAI, A. MITO, AND M. KATAYAMA, Chem. Phys. Lett. 118, 600-603 (1985).
- 30. A. STAHN, H. SOLKA, H. ADAMS, AND W. URBAN, Mol. Phys. 60, 121-128 (1987).
- 31. R. ANGSTL, H. FINSTERHÖLZL, H. FRUNDER, D. ILLIG, D. PAPOUŠEK, K. NARAHARI RAO, H. W. SCHRÖTTER, AND Š. URBAN, J. Mol. Spectrosc. 114, 454–472 (1985).

#### ZEISBERGER AND RUOFF

- 32. G. DI LONARDO, L. FUSINA, AND J. W. C. JOHNS, J. Mol. Spectrosc. 104, 282-301 (1984).
- 33. L. W. PINKLEY, K. NARAHARI RAO, G. TARRAGO, G. POUSSIGUE, AND M. DANG-NHU, J. Mol. Spectrosc. 68, 195-222 (1977).
- 34. J. DUPRÉ-MAQUAIRE, J. Mol. Spectrosc. 101, 319-324 (1983).
- 35. J. DUPRÉ-MAQUAIRE AND G. TARRAGO, J. Mol. Spectrosc. 96, 156-169 (1982).
- 36. E. HIROTA, J. Mol. Spectrosc. 37, 20-32 (1971).
- 37. Y. KAWASHIMA AND A. P. COX, J. Mol. Spectrosc. 64, 319-329 (1977).
- 38. J. G. SMITH, Mol. Phys. 32, 621-645 (1976).
- 39. M. L. GRENIER-BESSON, J. Phys. Radium 21, 555-565 (1960).
- 40. J. L. DUNCAN, J. Mol. Spectrosc. 22, 247-261 (1967).
- C. BETRENCOURT-STIRNEMANN, G. GRANER, D. E. JENNINGS, AND W. E. BLASS, J. Mol. Spectrosc. 69, 179–198 (1978); G. GRANER, private communication.
- 42. S. G. W. GINN, S. REICHMAN, AND J. OVEREND, Spectrochim. Acta Part A 26, 291-296 (1970).
- 43. J. L. DUNCAN, J. Mol. Spectrosc. 60, 225-238 (1976).
- 44. T. F. ANDERSON, E. N. LASSETRE, AND D. M. YOST, J. Chem. Phys. 4, 703-707 (1936).
- 45. D. M. YOST, D. DEVAULT, T. F. ANDERSON, AND E. LASSETRE, J. Chem. Phys. 6, 424-425 (1938).
- 46. S. MAES, Cah. Phys. 14, 125-208 (1960).