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Infrared diode laser and microwave spectra and molecular structure of an unstable molecule, FBO

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The FBO molecule was generated by a dc discharge in a mixture of BF₃, O₂, and He and its vibration-rotation and rotation spectra were observed by using infrared diode laser spectroscopy and microwave spectroscopy, respectively. The v_1 B–O stretching mode of F¹¹BO and F¹⁰BO and the $v_1 + v_2 - v_2$ hot band of F¹¹BO were observed in the region 2050 to 2140 cm⁻¹. Subsequently, the pure rotational spectrum was observed for the following isotopic species: F¹¹BO, F¹⁰BO, F¹¹B¹⁸O, and F¹⁰B¹⁸O. The rotational, centrifugal distortion, and *l*-type doubling constants were determined from the observed spectra, and the partial r_s structure of FBO was calculated from r_s coordinates and the first moment equation to be r(F-B) = 1.2833(7) Å and r(B-O) = 1.2072(7) Å.

I. INTRODUCTION

More than ten linear triatomic molecules containing a boron atom, including some ionic species, have been detected in the gas phase: HBO,¹⁻³ ClBO,⁴ HBS,⁵⁻⁸ FBS,⁹ ClBS,¹⁰⁻¹³ BrBS,⁹ ClBSe,^{9,13} BO₂,¹⁴⁻²⁰ HBF⁺,²¹⁻²³ HBS⁺,²⁴⁻²⁶ FBS⁺,²⁷ClBS⁺,^{10,27} and so on. The FBO molecule has not been included in this list. This is probably because the XBO molecules (X = H, F, and Cl) have much shorter lifetimes than those of XBS. This unstable molecule, FBO, seems to be easily trimerized to (FBO)₃, as, in fact, detected by mass spectrometry^{28,29} and infrared spectroscopy.³⁰

The FBO monomer was first detected by Snelson³¹ in a low-temperature matrix. He assigned the spectrum observed in a neon matrix as follows: $v_2 = 502 \text{ cm}^{-1}$ and $v_1 = 2081 \text{ cm}^{-1}$ for F¹¹BO and $v_2 = 521 \text{ cm}^{-1}$ and $v_1 = 2151 \text{ cm}^{-1}$ for F¹⁰BO. (In the present paper we define the higher stretching mode to be v_1 .) Boyer³² carried out a shock-tube measurement of FBO using the reaction of BF₃ and O₂ in 95% Ar and observed the spectrum profile of FBO at 5 μ m region using a scanning IR spectrometer. An *ab initio* calculation was made by Thomson³³ to derive the molecular structure: r(F-B) = 1.256 Å and r(B-O) = 1.190 Å.

In the present study we aimed at detecting this shortlived molecule, FBO, in the gas phase in order to determine the molecular structure and other parameters for FBO precisely.

II. EXPERIMENTAL

A. Diode laser spectroscopy

The diode laser spectrometer used was the same as that reported earlier.^{34,35} The glow discharge cell employed was made of a 1 m long glass tube of 65 mm inner diameter. The effective path length was chosen to be about 10 m using a multiple reflection configuration. The FBO molecule was produced by an ac discharge in a mixture of BF₃, O₂, and He. In the present experiment the spectrum of FBO was observed with source frequency modulation instead of dis-

charge frequency modulation which was effective for the detection of HBO,¹ because in the case of FBO the precursor and also reaction products did not absorb strongly in the observed region. The optimal condition for the production of FBO was obtained when the partial pressures of BF₃, O₂, and He were 60, 290, and 750 mTorr, respectively. The cell was cooled to dry-ice temperature. The discharge current was about 300 mA. The observed wave numbers were calibrated using the OCS ν_3 band³⁶ as a standard and a vacuumspaced etalon as an interpolation device.

B. Microwave spectroscopy

The source frequency modulation microwave spectrometer employed was described in detail in Refs. 37, 38, and 35. The FBO molecule was generated by a dc discharge in a BF₃ and O_2 mixture inside a free space cell, which had a diameter of 100 mm and length of 1 m. The optimum condition for the production of FBO was obtained when the partial pressures of BF₃ and O_2 were 25 and 25 mTorr, respectively. The discharge current was 40–50 mA. The cell was cooled to about -30 °C by flowing cold N₂ gas. The lifetime of FBO in the cell was found to be less than 1 s by observing the absorption intensity change after the discharge was turned off. This lifetime is longer than that in the infrared cell, presumably because the sample pressure is lower in the microwave than in the IR experiments.

The spectrum of $F^{10}BO$ was observed in natural abundance, whereas these of $F^{11}B^{18}O$ and $F^{10}B^{18}O$ were observed using the reaction of BF_3 with $^{18}O_2$. Spectra of other molecules were also observed while the electric discharge was on, but were not identified. A qualitative observation of the lifetime was found to be useful in discriminating FBO lines against others.

III. RESULTS

A. Infrared diode laser spectrum of FBO

According to the result of Snelson,³¹ we started to search for the absorption lines of the v_1 band of F¹¹BO near

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Transition

TABLE I. Diode laser spectra of the v_1 band of $F^{11}BO$ and $F^{10}BO$ (in cm⁻¹).

Transition

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close to twice the rotational constant expected for FBO. The frequency region between 2050 and $2150 \,\mathrm{cm}^{-1}$ was scanned. A part of the observed spectrum is shown in Fig. 1. In this region a number of absorption lines were observed and the strong lines were assigned to the v_1 and $v_1 + v_2 - v_2$ bands of $F^{11}BO$ and the v_1 band of $F^{10}BO$. For the v_1 band of $F^{11}BO 41$ lines were observed and the absence of a line at the band origin (2078.87 cm⁻¹) was confirmed, affirming the J assignment. However, it was not possible to make a J assignment for F¹⁰BO using the observed frequencies of 14 Pbranch transitions. Therefore, in order to confirm the J assignment the rotational and centrifugal distortion constants obtained from the microwave spectra were transferred. Table I lists the v_1 band spectral lines observed for $F^{11}BO$ and $F^{10}BO$. The lines of the $v_1 + v_2 - v_2$ hot band observed for $F^{11}BO$ are listed in Table II with their assignment.

 2081 cm^{-1} . A spectrum with a pattern of a linear molecule

was found: lines appeared every 0.6 cm^{-1} . This spacing is

B. Microwave spectra of FBO and its isotopic species

The search for the spectrum was started for the $J = 13 \leftarrow 12$ transition of F¹¹BO, which was expected to appear at 242 995 \pm 12 MHz according to the infrared data and was observed at 243 000.993 MHz. The line vanished immediately when the discharge was turned off, indicating that the species responsible for this line was of short life. This assignment was confirmed by observing the $J = 12 \leftarrow 11$, $J = 16 \leftarrow 15$, and $J = 20 \leftarrow 19$ transitions. The spectrum of F¹⁰BO was observed in a similar way, giving further support to the above assignment for F¹¹BO. The hyperfine structure splittings due to the boron nuclear quadrupole coupling were not observed in these transitions. Table III summarizes the transitions thus observed for F¹¹BO, F¹⁰BO, F¹¹B¹⁸O, and F¹⁰B¹⁸O in the ground vibrational state and Table IV lists those of F¹¹BO in the v_2 excited state.

The observed transition frequencies were analyzed by using the following equation for each vibrational state³⁹:

$$E = B_v [J(J+1) - l^2] - D_v [J(J+1) - l^2]^2$$

$$\pm 1/4 [q_v - q_v J(J+1)] (v_2 + 1) J(J+1).$$
(1)



FIG. 1. A part of the v_1 band and the $v_1 + v_2 - v_2$ band of $F^{11}BO$ recorded with source frequency modulation. The time constant of the phase sensitive detector used was 0.3 s.

1 I ansmon	008.	<u> </u>	Tanshion	003.	47
F ¹¹ BO			R(13)	2087.1773	- 3
P(42)	2049.2620	6	R(14)	2087.7398	- 4
P(41)	2050.0469	- 15	R (15)	2088.2999	4
P(40)	2050.8300	- 2	R(39)	2100.4972	6
P(36)	2053.9172	- 11	R (40)	2100.9523	- 9
P(35)	2054.6819	14	R(41)	2101.4053	- 4
P(34)	2055.4401	14	R(42)	2101.8528	- 12
P(20)	2065.6407	8	R(43)	2102.2773	6
P(19)	2066.3403	13	R(52)	2106.1052	- 4
P(18)	2067.0359	18	R (53)	2106.5078	3
P(13)	2070.4515	13	R(54)	2106.9046	- 6
P(12)	2071.1219	4	R(55)	2107.3003	17
P (11)	2071.7888	1	R(56)	2107.6873	- 4
P(10)	2072.4525	2			
P(9)	2073.1105	- 12	F ¹⁰ BO		
P (8)	2073.7667	5	P(62)	2101.8669	- 12
P(7)	2074.4184	- 3	P (57)	2106.3470	12
P (4)	2076.3483	- 10	P(56)	2107.2283	7
P(3)	2076.9837	- 11	P (41)	2119.9077	1
P(2)	2077.6162	- 2	P(40)	2120.7166	3
P (1)	2078.2434	- 6	P(39)	2121.5208	4
R (0)	2079.4870	- 2	P (34)	2125.4705	- 18
R (1)	2080.1024	- 4	P(33)	2126.2485	<u> </u>
R (2)	2080.7144	1	P(32)	2127.0211	2
R (3)	2081.3215	- 4	P(31)	2127.7875	- 8
R (4)	2081.9251	<u> </u>	P (30)	2128.5494	- 17
R (5)	2082.5248	- 3	P(26)	2131.5576	13
R(11)	2086.0378	- 3	P(25)	2132.2971	11
R (12)	2086.6111	16	P(24)	2133.0318	6

 $^{a}\Delta v = (v_{obs.} - v_{calc.}) \times 10^{4} \text{ cm}^{-1}.$

The last term of this equation, which includes a higher-order *l*-type doubling in q'_v , applies to only the $v_2 = 1$ state. This higher-order term was found necessary to reproduce the observed transition frequencies. The rotational, centrifugal distortion, and *l*-type doubling constants thus obtained are listed in Table V for the ground states of $F^{11}BO$, $F^{10}BO$,

TABLE II. Diode laser spectrum of the $F^{11}BO v_1 + v_2 - v_2$ band (in cm⁻¹).

Transition ^a	Obs.	$\Delta \nu^{b}$	Transition ^a	Obs.	$\Delta v^{\rm b}$
P(9) 1+	2065.3157	8	R(15) 1 +	2080.5706	- 7
P (9) 1 –	2065.3173	- 19	R(15) 1 -	2080.5405	22
P(8) 1 +	2065.9729	9	R(16) 1 +	2081.1296	<u> </u>
P(8) 1-	2065.9763	- 1	R(16) 1	2081.0941	- 3
P(7) 1+	2066.6248	- 4	R(17) 1 +	2081.6856	- 1
P(7) = 1 - 1	2066.6290	- 5	R(17) 1 -	2081.6461	- 3
R(9) 1 +	2077.1332	- 1	R(18) 1 +	2082.2373	3
R (9) 1 –	2077.1168	3	R(18) 1 -	2082.1944	2
R(10) 1 +	2077.7163	1	R(25) 1 +	2085.9849	- 4
R(10) 1 -	2077.6974	4	R(25) 1 -	2085.9137	- 11
R(11) 1 +	2078.2944	- 7	R(26) 1 +	2086.5048	- 2
R (11) 1 -	2078.2726	- 8	R(26) 1 -	2086.4304	5
R(13) 1 +	2079.4428	17	R(27) 1 +	2087.0200	- 6
R (13) 1 -	2079.4152	12	R(27) 1 -	2086.9407	- 2
R(14) 1 +	2080.0071	- 11	R(28) 1 +	2087.5338	15
R(14) 1 -	2079.9787	5	R(28) 1-	2087.4478	0

* l + and l - represent the upper and lower state of the l-type doubling, respectively.
 ^b See (a) in Table I.

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TABLE III. Observed microwave transitions of $F^{11}BO$, $F^{10}BO$, $F^{11}B^{18}O$, and $F^{10}B^{18}O$ in the ground state (in MHz).

	F ¹¹ BO		F ¹⁰ BO	
Transition	Obs.	$\Delta \nu^{a}$	Obs.	$\Delta \nu^{a}$
$J = 12 \leftarrow 11$	224 312.806	- 0.014	224 358.151	0.026
$J = 13 \leftarrow 12$	243 000.993	0.024	243 050.014	- 0.028
$J = 16 \leftarrow 15$	299 058.463	- 0.013	299 118.842	0.003
$J = 20 \leftarrow 19$	373 782.463	0.003	373 857.844	0.001
	F ¹¹ B ¹⁸ O		F ¹⁰ B ¹⁸ O	
Transition	Obs	Δv^{a}	Obs.	Δv^{a}
$J = 15 \leftarrow 14$	264 094.328	- 0.038	264 101.841	- 0.038
$J = 16 \leftarrow 15$	281 694.534	0.043	281 702.536	0.043
$J = 20 \leftarrow 19$	352 082.305	-0.006	352 092.232	- 0.006

 $^{a}\Delta v = v_{obs.} - v_{calc.}$

 $F^{11}B^{18}O$, and $F^{10}B^{18}O$, and the ν_2 state of $F^{11}BO$.

The infrared spectra of $F^{11}BO$ and $F^{10}BO$ were combined with the microwave data in the ground and $v_2 = 1$ states in the analysis, where the microwave transitions were given weights 10^5 to 10^6 times larger than those of the infrared transitions, according to the precision of each measurement. In the case of the v_1 band of $F^{10}BO$, the J assignment was made such that the centrifugal distortion constant in the v_1 state was close to the value of the ground state. Under this condition the standard deviation of the leastsquares fitting was minimum. The molecular constants obtained from the diode laser and microwave spectra are listed in Table VI.

C. Molecular structure

There are two problems to be solved for determining molecular structure of FBO precisely. The first problem is that the fluorine atom has no stable isotopic species and the second problem is that the boron atom is located close to the center of mass. Kraitchman's equation yields the r_s coordinates of the boron and oxygen atoms to be 0.103 58(11) and 1.317 44(2) Å, respectively. Then the r_s (B==O) length is 1.2139 Å, which is longer than those of related molecules by 0.008–0.012 Å: r_s (B==O) = 1.202 06(11) Å for HBO⁴⁰ and 1.206 22(21) Å for ClBO.⁴ This long bond length is ascribed to the r_s coordinate of boron atom being too small by the second reason mentioned above. Pierce's double substitution procedure⁴¹ was thus applied, which yielded the r_s coordinate of the boron to be 0.110 27(71) Å. The r_s (B==O)

TABLE IV. Observed transition frequencies of $F^{11}BO$ in the $v_2 = 1$ state (in MHz).

	$l + state^{a}$		l – state ^a	
Transition	Obs.	$\Delta \nu^{b}$	Obs.	$\Delta \nu^{b}$
$J = 12 \leftarrow 11$	225 169.942	- 0.011	224 814.785	0.008
$J = 13 \leftarrow 12$	243 939.394	0.007	243 544.651	- 0.001
$J = 16 \leftarrow 15$	300 200.534	0.005	299 727.168	- 0.009
$J = 20 \leftarrow 19$	375 208.752	- 0.002	374 617.416	0.003

* See footnote a in Table II.

^b See footnote a in Table III.

TABLE V. Molecular constants of FBO and its isotopic species in the ground and $v_2 = 1$ states.^a

Constant	F ¹¹ BO (0,0,0) state	F ¹⁰ BO (0,0,0) state	F ¹¹ B ¹⁸ O (0,0,0) state	F ¹⁰ B ¹⁸ O (0,0,0) state
B ₀ /MHz	9347.3834(30)	9349.2729(38)	8804.544(12)	8804.797(12)
Ď₀∕kHz	3.5273(50)	3.5335(62)	3.108(18)	3.114(18)
			F ¹¹ BO	
Co	onstant		(0.1.0) state	
B ,	/MHz	9	375.717 95(94)	
D,	/kHz		3.6226 (15)	
a	/MHz		14.8072 (18)	
	/Hz		30.2(31)	

^a Values in parentheses denote three standard deviations and apply to the last digits.

bond length is thus 1.2072(7) Å, which may be favorably compared with the r_s (B=O) bond lengths of HBO and ClBO.

The coordinate of the fluorine atom in FBO may be calculated by using either the first or the second moment equtions: -1.17306 Å and -1.17368 Å, respectively. Two values are close, but, because the first moment equation has been known to yield more reliable results than the second equation does, the first value was simply used to calculate the r(B-F) bond length to be 1.2833(7) Å.

The so-called r_0 structure was also calculated by choosing four pairs of isotopic species (two combinations, $F^{11}B^{16}O$ and $F^{10}B^{16}O$ and $F^{11}B^{18}O$ and $F^{10}B^{18}O$, were discarded since the moments of inertia of the two species were so close each other). The average values of the two bond lengths for four combinations are $r_0(B-F) = 1.2850(13)$ Å and $r_0(B=O) = 1.2061(14)$ Å, which agree well with the r_s values.

IV. DISCUSSION

Kawashima *et al.*⁴² attempted to observe the microwave spectra of FBO and ClBO using an ordinary waveguide cell without success, although the microwave transition of HBS was observed in the same cell. This evidence shows that the lifetimes of XBO (X = H, F, and Cl) are much shorter than those of XBS.

The v_1 band origins in a matrix reported in Ref. 31 are 2 cm⁻¹ higher than the present gas-phase value of F¹¹BO and F¹⁰BO. The *l*-type doubling constant q_2 may be expressed approximately by the formula $q_2 = 2.6B_e^2/\omega_2$.³⁹ When we use $\omega_2 = 502$ cm^{-1 31} and assume that B_e is equal to B_0 , q_2 is calculated to be 15.1 MHz for F¹¹BO, which may be favorably compared with the present exprimental value, 14.8072(18) MHz.

A comparison of r(B-F) = 1.317(2) Å in BH₂F⁴³ and 1.311(5) Å in BHF₂⁴⁴ with the present r(B-F) value reveals that the B-F bond length is decreased as the hybridization of boron changes from sp^2 to sp. This decrease is similar to that in r(B-Cl); the bond lengths $r_s(B-Cl) = 1.7389(12)$ Å in BH₂Cl⁴⁵ and 1.735(14) Å in BHCl₂⁴⁶ may be compared with $r_s(B-Cl) = 1.6827$ Å in ClBO,⁴ i.e., a decrease of 0.056 Å. These bond shortenings also occur in r(B-H) of HBO⁴⁰

TABLE VI. Rotational constants, centrifugal distortion constants, and v_1 and $v_1 + v_2 - v_2$ band origins of FBO (in cm⁻¹).^a

	F		¹ BO	F ¹	°BO
Constant	t (0,	.0,0) state	(1,0,0) state	(0,0,0) state	(1,0,0) state
B	0.311	795 10(12)	0.309 797 3(13)	0.311 858 13(15)	0.309 520 1(48)
10 ⁶ D	0.117	66(20)	0.120 64(49)	0.117 86(25)	0.119 0(12)
ν_0			2078.867 6(6)		2149.284 8(38)
				F ¹¹ BO	
Cor	nstant	(0,1,0) st	ate	(1,1,0) state	
	B	0.312 740	243(85)	0.310 755 2(78	3)
10	0° <i>D</i>	0.120 84(14)	0.119 6(84)	
1	$0^3 q$	0.493 93(17)	0.557 2(21)	
10° <i>q</i> ',	•	1.01(28)		•••	
	vo			2071.086 9(12)

*See footnote a in Table V.

(0.02–0.02 Å), in r(B-Cl) of ClBS¹¹ (0.047 Å), and in r(C-B) of CH₃BS¹¹ (0.065 Å).

It is interesting to note that the r_e (B–O) = 1.2045 Å in the BO radical⁴⁷ is close to r(B=O) in FBO, whereas the r_e (B–F) = 1.2625 Å in the BF radical⁴⁸ is shorter than that in FBO by 0.021 Å.

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