

Fourier Transform Spectroscopy of the $A^1\Pi-X^1\Sigma^+$ Transition of BH and BD

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The $A^1\Pi-X^1\Sigma^+$ transitions of BH and BD were recorded in emission near 4330 Å by Fourier transform spectroscopy. For BH improved line positions and molecular constants were determined from the analysis of the data. New bands of BD were found in our spectra. © 1991 Academic Press, Inc.

INTRODUCTION

The spectrum of the BH molecule in the visible and ultraviolet region was recorded by Lochte-Holtgreven and van der Vleugel (1), Thunberg (2), Almy and Horsfall (3), Douglas (4), and Chrétien and Miescher (5). Analysis of these spectra showed 4300 Å ($A^1\Pi-X^1\Sigma^+$), 3700 Å ($b^3\Sigma^- - a^3\Pi$), 3400 Å ($B^1\Sigma^+ - A^1\Pi$), 3100 Å ($C^1\Sigma^+ - A^1\Pi$), and 1920 Å ($B^1\Sigma^+ - X^1\Sigma^+$) band systems.

The most extensive spectroscopic measurements were made by Bauer *et al.* (6), who obtained the absorption spectrum of BH by the flash photolysis of borine carbonyl, H_3BCO . A number of new electronic transitions were found and most of the upper electronic states were Rydberg states. A value of ionization potential of 9.77 eV was derived. Johns *et al.* (7) discovered a new state, $C'^1\Delta$, during their improved measurements of the $A^1\Pi-X^1\Sigma^+$ system. From this experimental work, four vibrational levels in each the $X^1\Sigma^+$, the $A^1\Pi$, and the $B^1\Sigma^+$ states as well as three vibrational levels of the $C'^1\Delta$ state were found.

The radiative lifetime of the $A^1\Pi$ state has also been measured (8–12). Thompson and Dalby (13) measured the dipole moments of the $X^1\Sigma^+$ and $A^1\Pi$ states of BH to be 1.27 D and 0.58 D, respectively. Pianalto *et al.* observed the infrared vibration-rotation emission spectrum of BH (14).

Boron deuteride, BD, has however, received relatively little attention. The $A^1\Pi-X^1\Sigma^+$ system was recorded by Thunberg (2) at moderate resolution and the $B^1\Sigma^+ - X^1\Sigma^+$ and other vacuum ultraviolet transitions were studied by Bauer *et al.* (6).

BH, with only six electrons, is one of the simplest molecules and has been the subject of numerous theoretical investigations. A few of the recent calculations predict the dissociation energy (D_0) of BH (15–17) to be about 81.5 kcal/mole while others predict the $A^1\Pi$ lifetimes (12–18). BH is often used to test and verify new ab initio techniques (for example, see Refs. (19–24)).

The $A^1\Pi$ state is of considerable interest to both spectroscopists and quantum chemists because it has a barrier to dissociation. Purely ab initio potential curves are

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available (17, 18, 25) and occasionally these curves are improved by combination with experimental data (11, 26).

The present work on BH accidentally arose from an investigation aimed at obtaining spectra of BC (27). The BD spectrum was obtained by adding D_2 gas to the system. The analysis of these new spectra has led to the identification of new vibrational levels of BD.

EXPERIMENTAL DETAILS

The BH molecule was made in a hollow cathode discharge. In this experiment the B_4C composite-wall hollow cathode was operated at 300 mA current with a flow of 1.2 Torr of Ar gas (27). No hydrogen was added so the H atoms for the production of BH might possibly come from the dissociation of trace amounts of water vapor in the system.

The emission from the hollow cathode was observed with the McMath Fourier transform spectrometer operated by the National Solar Observatory at Kitt Peak. Twenty-two scans were coadded in 1.5 hr of integration with an unapodized resolution of 0.06 cm^{-1} . A Corion 6000-Å blue pass filter limited the wavelength response of the RCA 31034 photomultiplier detectors to approximately 3800–6000 Å.

After the accidental production of BH, we decided to make BD by the addition of 35 m Torr of D_2 gas to the hollow cathode discharge. The cathode was operated under the same conditions as in the above experiment. Thirty-three scans were coadded in 1.5 hr of integration. A prism monochromator, acting as a filter and a 6000-Å blue pass filter limited the frequency range to 21 700–24 000 cm^{-1} . Both spectra were calibrated to an absolute accuracy of better than $\pm 0.002\text{ cm}^{-1}$ with the Ar^+ atomic line positions of Norlen (28).

RESULTS AND DISCUSSION

The ground electronic states of BH and BD arise from the electron configuration:

$$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 \cdots X^1\Sigma^+.$$

The two lowest energy excited electronic configurations are

$$(1s\sigma)^2(2s\sigma)^2 2p\sigma 2p\pi \cdots A^1\Pi, a^3\Pi \\ (1s\sigma)^2(2s\sigma)^2(2p\pi)^2 \cdots b^3\Sigma^-, B^1\Sigma^+, \text{ and } C^1\Delta.$$

All the electronic states arising from these low-lying configurations have been experimentally identified for BH.

The 0–0, 1–1, and 2–2 vibrational bands of the $A^1\Pi-X^1\Sigma^+$ transition have been seen for ^{11}BH . The bandhead of the Q -branch for the 0–0 band is displayed in Fig. 1. For ^{11}BD , in addition to the above bands the 3–3 band was also observed in the emission spectrum. The Q -head of the 0–0 band of ^{11}BD is shown in Fig. 2. All of the R -branches form bandheads, but only the Q -branch of the 0–0 band forms a head.

The line positions were determined from the spectra by the data-reduction program, PC-DECOMP. This program fits the spectral features to Voigt lineshape functions to determine the peak positions. The measured line positions for ^{11}BH and ^{11}BD are listed in Tables I and II. The transitions for BH for all of the observed bands were

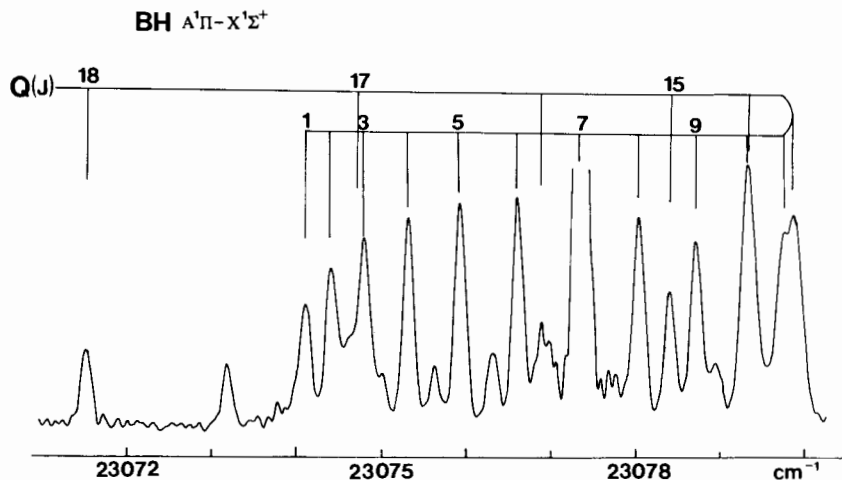


FIG. 1. A portion of the Q -branch of the 0-0 band of the $A^1\Pi-X^1\Sigma^+$ transition of BH near the bandhead.

easily assigned with the help of Johns *et al.*'s (7) work. For BD, the rotational lines for the 0-0 and 1-1 bands were assigned with the help of Thunberg's work (2), but the 2-2 and 3-3 bands are new.

The rotational line positions of BH and BD were fit to the customary energy level expression in each electronic state:

$$F(J) = \nu_0 + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 + L [J(J+1)]^4 \pm \delta_{1A} J(J+1) [q_v + q_{Dv} J(J+1)] / 2. \quad (1)$$

Approximate weights for the least-squares fit were chosen for each line on the basis of the signal-to-noise ratio as well as freedom from blending. The spectroscopic con-

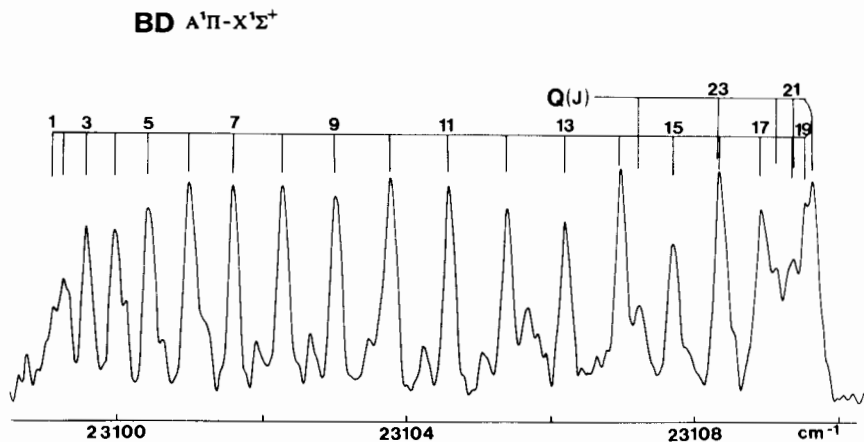


FIG. 2. A portion of the Q -branch of the 0-0 band of the $A^1\Pi-X^1\Sigma^+$ transition of BD near the bandhead.

TABLE I

Rotational Line Positions^a Measured for ^{11}BH (in cm^{-1})

0 - 0 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					23097.810	-5
1			23074.117	3	23121.849	7
2	23026.969	5	23074.414	19	23146.019	7
3	22003.859	3	23074.791	-12	23170.276	-4
4	22981.031	-4	23075.320	5	23194.595	2
5	22958.515	-2	23075.933	-7	23218.894	-3
6	22936.301	-7	23076.609	-12	23243.133	4
7	22914.410	2	23077.358	20	23267.217	5
8	22892.810	1	23078.040	-12	23291.097	-4
9	22871.526	22	23078.716	-7	23314.689	3
10	22850.471	3	23079.297	-2	23337.883	-6
11	22829.681	6	23079.714	-6	23360.606	-7
12	22809.100	12	23079.931	7	23382.757	3
13	22788.670	7	23079.841	9	23404.181	-17
14	22768.361	18	23079.371	9	23424.810	-6
15	22748.064	4	23078.412	-2	23444.458	-14
16	22727.744	10	23076.867	-11	23462.990	-21
17	22707.275	7	23074.636	9	23480.239	-21
18	22686.558	7	23071.523	4	23496.023	-8
19	22665.440	-11	23067.380	-8	23510.103	-5
20	22643.788	-24	23062.041	-4	23522.261	11
21	22621.439	-19	23055.280	5	23532.195	8
22	22598.179	0	23046.834	3	23539.628	17
23	22573.743	8	23036.414	-16	23544.176	0
24	-		23023.721	-25	23545.476	-9
25	22520.188	-2	23008.278	-128		
26	22490.398	2				

1 - 1 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					22913.998	0
1			22891.132	1	22935.889	-1
2	22845.702	66	22890.110	-8	22957.265	1
3	22822.056	6	22888.556	-19	22978.061	2
4	22798.108	19	22886.473	-0	22998.206	-2
5	22773.745	-4	22883.775	1	23017.625	-4
6	22749.020	-1	22880.425	-1	23036.229	-4
7	22723.895	18	22876.376	1	23053.906	-8
8	22698.287	2	22871.528	-16	23070.545	-12
9	22672.196	4	22865.870	26	23086.026	-2
10	22645.542	6	22859.179	3	23100.185	7
11	22618.244	9	22851.459	39	23112.848	10
12	22590.192	3	22842.439	2	23123.808	-9
13	22561.277	-4	22832.085	18	23132.901	3
14	22531.362	-4	22820.119	-2	23139.811	-21
15	22500.277	5	22806.374	-9	23144.328	-12
16	22467.831	35	22790.593	-4	23146.186	89
17	22433.736	36	22772.470	0	23144.737	4
18	22397.696	-2	22751.663	5	23139.811	-10
19	22359.500	41	22727.757	-6		
20	22318.594	0				

2 - 2 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					22569.666	-4
1			22547.600	-29	22588.612	14
2			22544.492	8	22605.914	9
3	22478.849	12	22539.701	-15	22621.515	12
4	22452.425	-13	22533.267	2	22635.280	2
5	22424.508	-17	22525.045	-2	22647.078	-18
6	22395.046	3	22514.957	-1	22656.802	9
7	22363.892	-18	22502.867	3	22664.183	5
8	22331.029	11	22488.603	-2	22669.030	3
9	22296.238	9	22471.977	-6	22671.063	-5
10	22259.365	-2	22452.754	-5	22669.969	-12
11	22220.215	-0	22430.654	12	22665.347	-34
12	22178.458	-44	22405.275	2	22656.796	2
13	22133.885	-0	22376.200	-10		

^a Observed-Calculated line positions using the constants of Table III.

TABLE II
Rotational Line Positions Measured for ^{11}BD (in cm^{-1})

0 - 0 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					23112.055	30
1			23099.093	-9	23125.158	-1
2	23073.329	-1	23099.282	-16	23138.401	9
3	23060.698	2	23099.556	-34	23151.712	0
4	23048.192	-13	23099.972	-1	23165.101	-4
5	23035.854	-7	23100.470	28	23178.552	-3
6	23023.677	8	23101.016	26	23192.044	-2
7	23011.620	-9	23101.606	-4	23205.550	-9
8	22999.736	-6	23102.289	-3	23219.095	20
9	22987.999	-5	23103.014	-11	23232.547	-24
10	22976.438	21	23103.762	-35	23246.058	32
11	22964.960	-11	23104.592	-2	23259.410	-4
12	22953.651	-12	23105.392	-7	23272.709	-2
13	22942.482	-2	23106.180	-16	23285.895	8
14	22931.423	2	23106.967	0	23298.877	-36
15	22920.500	35	23107.691	4	23311.775	18
16	22909.599	-1	23108.343	8	23326.747	-10
17	22898.813	5	23108.893	7	23348.844	5
18	22888.059	-11	23109.306	-2	23360.588	4
19	22877.357	-5	23109.554	-19	23371.937	-11
20	22866.676	15	23109.648	3	23382.895	12
21	22855.963	26	23109.477	-10	23393.330	-4
22	22845.196	39	23109.074	18	23403.237	-7
23	22834.285	-0	23108.293	-16	23412.584	-13
24	22823.276	-4	23107.211	16	23421.178	-9
25	22812.046	-50	23105.664	6	23429.080	-1
26	22800.681	-2	23103.613	-24	23436.171	24
27	22788.967	-15	23101.030	-37	23442.332	30
28	22776.919	-11	23097.881	6	23447.446	-4
29	22764.445	-14	23093.963	-15	23451.488	2
30	22751.488	-2	23089.293	4	23454.323	26
31	22737.951	15	23083.688	-21	23455.754	1
32	22723.705	5	23077.148	20	23455.658	-67
33	22708.697	21	23069.389	-41	23454.200	143
34	22692.733	-14	23060.408	-73	23450.249	-337
35	22675.732	-45				
36	22657.510	-125				
37	22637.882	-269				

1 - 1 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					23002.074	-5
1			22989.486	-4	23014.409	-15
2			22989.223	-9	23026.633	-4
3	22951.593	-27	22988.816	24	23038.680	-26
4	22938.770	-5	22988.304	-4	23050.696	85
5	22925.835	-9	22987.621	-7	23062.345	8
6	22912.827	-1	22986.790	0	23073.871	13
7	22899.725	-3	22985.789	9	23085.162	8
8	22886.514	-12	22984.586	1	23096.205	9
9	22873.249	18	22983.194	9	23106.967	11
10	22859.850	23	22981.579	17	23117.405	2
11	22846.306	6	22979.691	-11	23127.520	19
12	22832.652	16	22977.565	17	23137.230	18
13	22818.832	16	22975.109	5	23146.485	-10
14	22804.827	9	22972.321	-2	23155.300	-5
15	22790.608	-5	22969.180	11	23163.582	-11
16	22776.176	1	22965.590	-13	23171.290	-13
17	22761.477	12	22961.562	-16	23178.379	1
18	22746.440	-6	22957.030	-14	23184.744	-10
19	22731.035	-38	22951.921	-24	23190.335	-26
20	22715.241	-55	22946.195	-25	23195.134	12
21	22699.014	-42	22939.773	-26	23198.932	-24
22	22682.275	-19	22932.613	5	23201.769	-3
23	22664.898	-38	22924.590	26		
24	22646.906	9	22915.616	40		
25	22628.116	7	22905.578	35		
26	22608.487	19	22894.359	1		
27			22881.931	33		
28			22868.002	-28		
29			22852.457	-150		

TABLE II—Continued

2 - 2 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					22818.519	-47
1			22806.304	-2	22829.921	-19
2			22805.402	-6	22840.847	-12
3	22768.766	-14	22804.051	-7	22851.279	-26
4	22755.306	11	22802.220	-10	22861.259	3
5	22741.404	7	22799.940	13	22870.689	4
6	22727.098	18	22797.133	6	22879.552	-11
7	22712.304	-31	22793.822	15	22887.863	8
8	22697.143	-5	22789.966	20	22895.531	8
9	22681.501	-1	22785.532	21	22902.508	-16
10	22665.396	21	22780.466	-3	22908.801	-7
11	22648.748	7	22774.792	11	22914.354	31
12	22631.575	11	22768.398	-3	22918.988	-20
13	22613.808	-5	22761.275	-2	22922.781	-12
14	22595.423	-5	22753.335	-17	22925.574	-33
15	22576.341	-28	22744.539	-23	22927.385	19
16	22556.574	2	22734.806	-24		
17	22535.977	0	22724.044	-32		
18	22514.507	10	22712.213	4		
19	22492.051	5	22699.126	1		
20			22684.725	15		
21			22668.864	25		
22			22651.382	10		
23			22632.131	-25		

3 - 3 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					22536.076	5
1			22524.167	10	22546.169	10
2			22522.277	39	22555.279	-42
3	22486.799	84	22519.552	13	22563.583	46
4	22472.074	-65	22515.822	11	22570.783	5
5	22456.674	19	22511.119	12	22576.970	-41
6	22440.263	13	22505.419	22		
7	22422.866	-32	22498.669	27	22586.316	29
8	22404.561	-10	22490.807	8	22589.240	14
9	22385.195	-38	22481.816	4		
10	22364.831	-7	22471.609	-7		
11	22343.349	19	22460.143	3		
12	22320.652	5	22447.383	-11		
13	22296.755	45	22432.955	-25		
14	22271.446	13	22417.070	-16		
15	22244.679	-30	22399.471	-8		
16	22216.378	-45	22380.041	27		
17			22358.529	6		
18			22334.820	-22		
19			22308.693	-11		

stants for the $A^1\Pi$ and $X^1\Sigma^+$ states provided by the fits are reported for ^{11}BH and ^{11}BD in Tables III and IV, respectively.

For BH the 0-0, 1-1, and 2-2 bands of the $A^1\Pi-X^1\Sigma^+$ transition were combined with the 1-0, 2-1, and 3-2 infrared rotation-vibration lines (14). All these rotational lines were fit simultaneously to extract the molecular constants in the ground and excited electronic states. The value for L in $v'' = 0$ was obtained by fitting the 0-0 band separately. For $v'' = 1$ and 2 levels this L_0 value ($-4.5 \times 10^{-12} \text{ cm}^{-1}$) was used. Infrared data are not available for ^{11}BD and nondiagonal bands were not observed so each band was fit separately. For the 0-0 band, the value for L'' was estimated ($-3.9 \times 10^{-13} \text{ cm}^{-1}$) from the isotopic relationship using the ^{11}BH value. The values for L were held fixed to the $v = 0$ values ($L' = -4.66 \times 10^{-12} \text{ cm}^{-1}$) in the $v = 1, 2,$ and 3 levels for both electronic states. Inspection of the values of the centrifugal distortion

TABLE III

Molecular Constants for the $A^1\Pi-X^1\Sigma^+$ Transition of ^{11}BH (in cm^{-1})

Constant	$v=0$	$v=1$	$v=2$
$X^1\Sigma^+$			
T_v	0	2269.22707(25)	4443.03454(71)
B_v	11.815745(43)	11.400844(37)	10.992633(60)
$10^3 D_v$	1.22305(50)	1.20106(36)	1.1800(11)
$10^8 H_v$	9.86(13)	10.052(16)	10.55(50)
$10^{12} L_v$	-4.5(10)	-4.5 ^a	-4.5 ^a
$A^1\Pi$			
T_v	23073.9708(22)	25160.8602(25)	26992.2261(46)
B_v	11.906298(81)	11.16801(12)	10.22817(38)
$10^3 D_v$	1.43853(74)	1.5986(15)	2.0179(92)
$10^8 H_v$	5.00(19)	-6.39(62)	-20.0(81)
$10^{11} L_v$	-6.88(16)	-18.71(87)	-164(23)
$10^2 q$	3.7364(28)	3.4736(39)	3.0301(95)
$10^5 q_D$	-1.6846(63)	-1.997(13)	-1.817(67)

^a Fixed to the $v=0$ value.

TABLE IV

Molecular Constants for the $A^1\Pi-X^1\Sigma^+$ Transition of ^{11}BD (in cm^{-1})

Constant	$v=0$	$v=1$	$v=2$	$v=3$
$X^1\Sigma^+$				
B_v	6.45135(17)	6.28516(22)	6.12095(39)	5.9478(16)
$10^4 D_v$	3.6271(29)	3.588(35)	3.564(12)	2.38(12)
$10^8 H_v$	1.573(15)	1.603 ^a	1.683 ^a	1.738 ^c
$10^{13} L_v$	-3.9 ^a	-3.9 ^b	-3.9 ^b	-3.9 ^b
$A^1\Pi$				
T_{vv}	23099.0025(33)	22989.6174(44)	22806.7531(48)	22525.075(10)
B_v	6.50651(18)	6.22659(23)	5.90251(41)	5.4942(18)
$10^4 D_v$	4.1788(36)	4.432(42)	4.927(14)	4.61(14)
$10^9 H_v$	8.17(36)	-8.59(23)	-42.56(79)	-135.5(56)
$10^{12} L_v$	-4.66(15)	-4.66 ^b	-4.66 ^b	-4.66 ^b
$10^2 q$	1.1096(19)	1.0451(48)	1.0060(95)	9.79(25)
$10^6 q_D$	-2.652(23)	-2.71(11)	-4.57(42)	1.97(31)

^a Calculated from the corresponding ^{11}BH values using the isotopic relationships.^b Fixed to the $v=0$ value.^c Extrapolated value.

constants of the excited $A^1\Pi$ state (Tables III and IV) indicates that the usual power series expansion (Eq. (1)) is a poor representation of the data.

Boron has two stable isotopes, ^{10}B and ^{11}B (20 and 80%). Rotational lines associated with ^{10}BH were measured for the 0-0 and 1-1 bands. The BD lines were weaker than BH lines and the spectrum of the impurity molecule CD makes it difficult to measure the weaker ^{10}BD lines. As a result, most of the ^{10}BD lines were blended except for a few P -branch lines and only the 0-0 band was found. The measured lines are provided in Tables V and VI and they were fit to the same energy level expression (Eq. (1)) as in the case of ^{11}BH and ^{10}BD . The values for D and q_D were estimated from the isotopic relationships using the corresponding ^{11}BH and ^{11}BD values and were held fixed in the fit. The molecular constants for ^{10}BH and ^{10}BD are provided in Table VII.

Our Fourier transform emission data of BH show almost the same number of rotational lines in $v = 0, 1,$ and 2 levels of the $A^1\Pi$ state as in the emission spectrum obtained by Johns *et al.* (7). It is very clear that lines with $J' = 27, 21,$ and 14 are definitely missing in the bands with $v' = 0, 1,$ and $2,$ respectively. Lines with J' equal to one less than the figures given above are almost certainly present, although in some cases their intensity has already dropped sharply or they are unusually broadened. Rotational lines for the 3-3 band do not appear in the spectrum.

TABLE V
Rotational Line Positions Measured for ^{10}BH (in cm^{-1})

J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
0					23097.676	-52
1					23121.965	13
2					23146.307	-10
3	23002.976	-1			23170.741	-37
4	22979.923	-37	23075.012	-1	23195.248	-34
5	22957.241	-7	23075.627	13	23219.802	30
6	22934.884	37	23076.310	31	23244.171	-14
7	22912.752	-8	23076.979	1	23268.473	18
8	22890.997	12	23077.681	5	23292.481	-24
9					23316.312	52
10			23078.937	35	23339.648	16
11					23362.514	-20
18			23073.175	-21		
19			23070.091	-10		
20			23066.492	306		

1 - 1 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
3			22886.834	-67	22977.058	-25
4			22884.755	15	22997.353	4
5			22881.949	-18	23016.876	2
6	22746.135	-35	22878.571	35	23035.584	14
7			22874.458	67	23053.345	8
8	22694.976	17			23070.053	-14
9	22668.645	4				
10			22856.937	-15		
11			22849.024	-166		

TABLE VI
Rotational Line Positions Measured for ^{10}BD (in cm^{-1})

0 - 0 Band						
J	P(J)	O-C	Q(J)	O-C	R(J)	O-C
1					23125.192	-4
2					23138.621	-3
3					23152.117	-20
4	23047.105	26			23165.725	2
5	23034.550	5			23179.337	-28
6	23022.154	-9	23100.608	-33	23193.072	28
7	23009.921	-15	23101.246	-15	23206.728	-16
8	22997.862	-3	23101.953	10	23220.467	24
9			23102.676	-1		
10	22974.183	-5	23103.483	33		
11			23104.262	12		
12			23105.072	12		
13			23105.924	58		
14			23106.630	-21		
15			23107.360	-34		
16			23108.048	-29		

The reason for observing $v' = 3$ of the $A^1\Pi$ state in absorption but not in emission is simply because the emission breaks off substantially below the top of the potential barrier as a result of tunneling through the barrier. This tunneling broadens the levels and shortens the lifetimes enough to prevent emission. The height of the potential barrier to dissociation is estimated to be about 1.9 ± 0.2 kcal/mole (17).

For BD, emission from $v' = 3$ in the $A^1\Pi$ state was observed. Clearly $J' = 36, 29, 23,$ and 18 levels exist for $v' = 0, 1, 2,$ and $3,$ respectively. However, due to the poor

TABLE VII
Molecular Constants for the $A^1\Pi-X^1\Sigma^+$ Transition of ^{10}BH and ^{10}BD (in cm^{-1})

Constant	^{10}BH		^{10}BD
	$v=0$	$v=1$	$v=0$
$X^1\Sigma^+$			
B_v	11.91502(52)	11.49288(96)	6.54868(59)
$10^3 D_v$	1.243 ^a	1.221 ^a	0.3746 ^a
$A^1\Pi$			
T_{vv}	23073.6860(76)	22890.048(17)	23098.6496(95)
B_v	12.00484(50)	11.25334(98)	6.60400(60)
$10^3 D_v$	1.462 ^a	1.625 ^a	0.4314 ^a
$10^2 q$	3.848(13)	3.605(32)	1.114(20)
$10^5 q_D$	-1.685 ^a	-2.065 ^a	-2.694 ^a

^a Fixed to the values estimated from isotopic relationships.

signal-to-noise ratio in these high J lines, it is hard to estimate a maximum J value.

In order to find the equilibrium molecular parameters the rotational lines of ^{11}BH were fit to a Dunham-type expression (29). To account for the Λ -type doubling in the $A^1\Pi$ state the customary Dunham expression was modified:

$$T_{vJ} = \sum_{ij} (Y_{ij} \pm Q_{ij}) \left(v + \frac{1}{2} \right)^i [J(J+1)]^j, \quad (2)$$

where + corresponds to e and - to f parity levels. The measured line positions for 0-0, 1-1, and 2-2 bands of the $A^1\Pi-X^1\Sigma^+$ transition for ^{11}BH were fit with the infrared data from the rotation-vibration spectrum (14) to the above expression (Eq. (2)). Y'_{30} ($\sim \omega_e y_e$) was fixed to the value given by Johns *et al.* (7), 15.82 cm^{-1} , for the excited state. The Dunham coefficients for both electronic states are given in Table VIII. The r_e values calculated from the Y_{01} values of Table VIII are $1.223320(8) \text{ \AA}$ and $1.232168(2) \text{ \AA}$ for the $A^1\Pi$ and $X^1\Sigma^+$ states, respectively.

The BD spectrum was limited to the $\Delta v = 0$ sequence. A new spectrum was recorded with same experimental conditions with a wider band pass filter in order to see bands with $\Delta v = \pm 1$. However, this new spectrum did not yield any new bands. An attempt was made to fit the BD data to a Dunham expression by fixing the vibrational constants using isotopic relations but this was not successful.

TABLE VIII

The Dunham Coefficients for the $A^1\Pi$ and $X^1\Sigma^+$ States of ^{11}BH (in cm^{-1})

Dunham coefficient	$X^1\Sigma^+$	$A^1\Pi$
Y_{00}	0.0	23135.4376(37)
Y_{10}	2366.7296(16)	2251.4577(68)
Y_{20}	-49.33983(99)	-56.5725(27)
Y_{30}	0.36227	-15.82 ^a
Y_{01}	12.025755(45)	12.20035(15)
Y_{11}	-0.421565(22)	-0.53767(30)
Y_{21}	0.0033195(61)	-0.10070(13)
$10^3 Y_{02}$	-1.23493(45)	-1.4577(16)
$10^5 Y_{12}$	2.247(12)	9.86(37)
$10^4 Y_{22}$	-	-1.224(18)
$10^8 Y_{03}$	9.98(10)	2.32(58)
$10^7 Y_{13}$	-	1.38(15)
$10^7 Y_{23}$	-	-1.631(73)
$10^{11} Y_{04}$	-5.18(75)	-6.96(11)
$10^2 Q_{01}$	-	3.8263(53)
$10^3 Q_{11}$	-	-1.406(97)
$10^4 Q_{21}$	-	-6.38(29)
$10^5 Q_{02}$	-	-1.532(11)
$10^6 Q_{12}$	-	-3.20(17)

^a Fixed to the value in ref. 7.

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