Vibration–Rotation Spectrum of BH $X^1\Sigma^+$ by Fourier Transform Emission Spectroscopy

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The vibration–rotation emission spectrum of the BH $X^1\Sigma^+$ state was observed with the McMath Fourier transform spectrometer at Kitt Peak. The 1–0, 2–1, and 3–2 bands were observed in a microwave discharge of B_2H_6 in He. Spectroscopic constants of the individual vibrational levels and equilibrium molecular constants were determined. An RKR potential curve was calculated from the equilibrium constants. © 1988 Academic Press, Inc.

INTRODUCTION

The spectrum of the BH molecule was first studied in 1931 by Lochte-Holtgreven and van der Vleugel (*1*). Two systems of emission bands, the $A^1\Pi$–$X^1\Sigma$ system near 4330 Å and the $b^3\Sigma$–$a^3\Pi$ system near 3700 Å, were observed in this work.

Since then, several additional spectroscopic studies on BH have been undertaken (*2–5*). The most extensive work was done in the near and vacuum ultraviolet regions of the spectrum by Bauer, *et al.* (*4*) and by Johns *et al.* (*5*). Additional experimental work on BH includes a measurement of the dipole moments in the $A^1\Pi$ and $X^1\Sigma^+$ states (*6*) and the measurements of the radiative lifetime in the $A^1\Pi$ state (*7–9*).

Presented here is the first vibration–rotation spectrum of BH. The spectrum was recorded in emission from a microwave discharge of diborane in helium with a Fourier transform spectrometer.

Since the BH molecule has only six electrons, the system is frequently used to test the accuracy of various *ab initio* theoretical methods. For example, using the *ab initio* CASSCF technique, Jaszunski *et al.* (*10*) mapped out the $B^1\Sigma^+$, $A^1\Pi$, and $X^1\Sigma^+$ potential energy curves of BH. Luh and Stwalley (*11*) combined these potential curves with experimentally based RKR potential energy turning points to obtain accurate hybrid potential energy curves. Botschwina (*12*) calculated many spectroscopic properties for the $X^1\Sigma^+$ state of BH using *ab initio* (SCEP-CEPA) methods in order to test the adequacy of such methods for use with the HBF^+ molecule. There have been a large number of additional theoretical calculations on BH (*13–25*) and our list of references is by no means complete.

EXPERIMENTAL DETAILS

The BH molecule was observed during an attempt to make BH_3. The boron containing molecules were produced in a microwave discharge of a mixture of approxi-

mately 1 Torr He and 0.016 Torr diborane (B_2H_6). The mixture was passed through an electrodeless quartz discharge tube and the discharge was driven by a 2450-MHz microwave oscillator. The diborane used in the discharge was prepared by adding sodium borohydride ($NaBH_4$) to heated polyphosphoric acid under vacuum.

The emission from the discharge tube was observed with the McMath Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak. Four scans were coadded in approximately 30 min of integration. The unapodized resolution was set to 0.02 cm^{-1}. InSb detectors and a silicon filter limited the band-pass region to approximately 1800 to 9000 cm^{-1}. The He atomic line at 5346.9261 cm^{-1} was used to calibrate the wavenumber scale with an absolute accuracy of about ±0.002 cm^{-1}. The wavenumber of this line was determined from a previously recorded spectrum which contained both He and Ar.

TABLE I

The Observed Line Positions for the Vibration–Rotation Spectrum of BH $X^1\Sigma^+$ (in cm^{-1})

J''	$P(J'')$	$\Delta\nu$ [a]	$R(J'')$	$\Delta\nu$
		1-0 Band		
0	-		2292.0226	-0.0010
1	2245.6007	0.0006	2313.9611	-0.0010
2	2221.1747	0.0014	2335.0148	0.0009
3	2195.9750	-0.0009	2355.1511	-0.0003
4	2170.0391	0.0009	2374.3478	-0.0002
5	2143.3900	-0.0006	2392.5762	-0.0013
6	2116.0647	0.0011	2409.8158	0.0009
7	2088.0859	-0.0021	2426.0366	0.0004
8	2059.4945	0.0000	2441.2194	0.0012
9	2030.3159	0.0023	2455.3379	-0.0010
		2-1 Band		
0	-		2195.7896	0.0015
1	2151.0131	0.0024	2216.9235	-0.0004
2	2127.4232	-0.0030	2237.1874	0.0001
3	2103.0828	-0.0005	2256.5511	-0.0003
4	2078.0125	0.0007	2274.9894	-0.0005
5	2052.2411	-0.0006	2292.4752	-0.0021
6	2025.8035	0.0005	2308.9905	0.0017
7	1998.7280	0.0020	2324.4993	-0.0012
		3-2 Band		
2	-		2141.5784	0.0019
3	2012.3338	0.0014	2160.1684	-0.0064
4	1988.1081	-0.0003	2177.8702	0.0062
5	1963.1988	0.0021	2194.6328	0.0118
6	1937.6215	-0.0069	2210.4280	0.0043
7	1911.4273	-0.0079	2225.2492	-0.0022

[a] Observed - Calculated line positions using the constants of Table II.
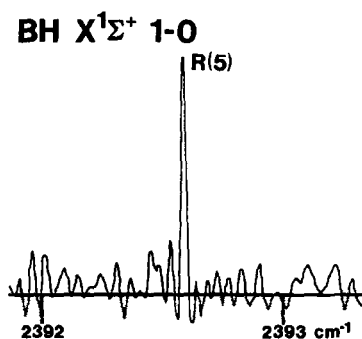
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FIG. 1. The $R(5)$ line of the fundamental (1–0) vibration–rotation band of BH.

RESULTS AND DISCUSSION

The interferogram was transformed by G. Ladd to produce the spectrum. The line positions were determined from the spectrum by a data-reduction program, DECOMP, developed at Kitt Peak. The DECOMP program fits the spectral features with Voigt lineshape functions to determine the peak positions. Lines with signal-to-noise of less than ∼2 were measured by eye. The absolute accuracy and relative precision of the strong unblended lines is estimated to be ±0.002 cm^{-1}.

Forty-five lines from the vibration–rotation bands 1–0, 2–1, and 3–2 were observed and are listed in Table I. One of the strongest lines in the R branch is shown in Fig. 1. The strongest lines have a signal-to-noise ratio of around 10, while the weakest lines have a ratio of about 1.5. The observed linewidth of the BH lines was approximately 0.025 cm^{-1}. The transitions were assigned with the help of very good spectroscopic constants from the previous high-resolution optical study of BH by Johns et al. (5).

The molecular constants of Table II were determined from a nonlinear least-squares fit of all of the transition frequencies given in Table I. The four vibrational levels ($v = 0$–3) were fit simultaneously using the customary $^1\Sigma^+$ energy level expression. The rotational constant H_v for each of the four vibrational levels was held fixed to the values from Johns et al. (5). The molecular constants determined here agree well with the constants determined by Johns et al. (5), although ours are slightly more accurate.

TABLE II

Molecular Constants for BH $X^1\Sigma^+$ (in cm^{-1})

Constant	v=0	v=1	v=2	v=3
T_v	0.0	2269.22670(53)	4443.0344(11)	6523.6106(75)
B_v	11.815729(55)	11.400868(45)	10.992600(86)	10.58980(48)
$D_v \times 10^3$	1.22371(58)	1.20196(39)	1.1786(11)	1.1418(61)
$H_v \times 10^7$	1.125[a]	1.097[a]	0.91[a]	0.90[a]

[a] Held fixed to values of Johns et al. (Ref. (5)).

TABLE III

Equilibrium Molecular Constants
for BH $X^1\Sigma^+$ (in cm^{-1})

Constant[a]	Value
ω_e	2366.7275(28)
$\omega_e x_e$	49.3384(20)
$\omega_e y_e$	0.36194(42)
B_e	12.025542(77)
α_e	0.421516(46)
γ_e	0.003317(13)
$D_e \times 10^3$	1.2313(14)
$\beta_e \times 10^5$	-2.190(40)
$H_e \times 10^7$	0.873(99)
r_e (Å)	1.232179(3)

[a] As defined in Ref. (26), pp. 92, 107, and 108.

The lines of Table I were also fit to a $^1\Sigma^+$ Dunham-type (27) energy level expression to determine equilibrium molecular constants presented in Table III:

$$E_{vJ} = \Sigma Y_{kl}(v + 1/2)^k [J(J + 1)]^l.$$

The rotational constant H_e was allowed to vary and was determined in this fit. The

TABLE IV

RKR Turning Points for BH $X^1\Sigma^+$

v	E_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)
0.0	1172.6335	1.12036	1.37113
0.5	2319.3101	1.08069	1.43834
1.0	3441.8604	1.05255	1.49444
1.5	4540.5558	1.03030	1.54511
2.0	5615.6678	1.01174	1.59253
2.5	6667.4679	0.99579	1.63781
3.0	7696.2274	0.98177	1.68163
3.5	8702.2179	0.96928	1.72442
4.0	9685.7108	0.95801	1.76649

TABLE V

Rotational Constants Calculated from the Potential Curve of Table IV (in cm^{-1})

Constant	v=0	v=1	v=2	v=3	v=4
B_v	11.8159	11.4006	10.9924	10.5910	10.1960
$D_v \times 10^3$	1.230	1.207	1.185	1.161	1.138
$H_v \times 10^7$	1.08	1.06	1.04	1.02	1.01
$L_v \times 10^{11}$	-1.3	-1.4	-1.2	-1.3	-1.5

equilibrium constants of Table III were used to determine a Rydberg–Klein–Rees (RKR) (28) potential curve for the $X^1\Sigma^+$ state. Energies and turning points up to the fourth vibrational level determined from the RKR fit are presented in Table IV. An RKR potential curve for the $^1\Sigma^+$ state of BH was also calculated by Luh and Stwalley (11) using experimental constants of Johns et al. (5). The turning points and rotational constants calculated in the present work agree well with the RKR results determined previously.

Finally, the RKR points and the dissociation energy (D_0 = 3.42 eV (29)) of BH were input to Hutson's centrifugal distortion program (30) to calculate values of B, D, H, and L. The values of these constants for vibrational levels 0–4 are presented in Table V. Hutson's program predicts the experimental constants of Table II with reasonable accuracy. Note that the values for levels $v > 3$ in Table IV and V are extrapolations and not directly based on observed experimental data.

ACKNOWLEDGMENTS

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