The Spectra of Neutral and Ionized Boron Hydride

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The spectrum of boron hydride, as excited in the cathode of a Schüler lamp, consists of at least three systems, $^1\Pi \rightarrow {}^1\Sigma$ of BH, $^3\Sigma \rightarrow {}^3\Pi$ of BH, and a new system, $^2\Pi \rightarrow {}^2\Sigma$, due to BH⁺.

BH, $^1\Pi \rightarrow {}^1\Sigma$.—This system has been extended to include the (2,2) band. One is thereby enabled to refine the rotational and vibrational constants of the system and, from a study of dissociation by rotation, to fix the heat of dissociation (D_e) of the normal state at 3.60 ± 0.05 ev.

BH, $^3\Sigma \rightarrow {}^3\Pi$, (0,0) head at λ3694.—The fine multiplet structure of this system has been resolved and the transition, previously reported to be $^3\Pi \rightarrow {}^3\Sigma$, established as $^3\Sigma \rightarrow {}^3\Pi$. The $^3\Pi$ state is regular and near case b ($A/B = +0.47$).

BH⁺, $^2\Pi \rightarrow {}^2\Sigma$, (0,0) head at λ3766.—This system is the analog of the green bands of the isoelectronic molecule BeH. Application of the Hill and Van Vleck theory to the $^2\Pi$ state does not yield an A/B which is constant with increasing J. Refinement of the theory to include the rotational D term, along the lines suggested by Gilbert for $^3\Pi$ states, does not greatly improve the situation. The remaining discrepancy is probably due to unobservable $^2\Sigma$ doubling. The Λ type doubling has been evaluated and compared with theory with results very like those in BeH

THE spectrum of boron hydride was first studied by Lochte-Holtgreven and van der Vleugel[1] and by Paton and Almy.[2] Recently Thunberg[3] has investigated the spectrum, particularly the isotope effect in the singlet bands due to the two boron and two hydrogen isotopes. Photographs of the spectrum as excited in the hollow cathode discharge reveal several new features of the spectrum which are the subject of this paper. First, the $^1\Pi \rightarrow {}^1\Sigma$ system, of which the (0,0) and (1,1) bands have been reported, has been extended to include the (2,2) band. Each of the three bands, moreover, exhibits dissociation by rotation which enables the heat of dissociation to be fixed fairly accurately. Second, the fine structure of the triplet band, discovered by Lochte-Holtgreven and van der Vleugel, has been more clearly resolved than by them and the transition fixed as $^3\Sigma \rightarrow {}^3\Pi$, instead of $^3\Pi \rightarrow {}^3\Sigma$, as reported. The molecular constants, including the electronic coupling coefficient in the $^3\Pi$ state, have been determined. Third, a new system, $^2\Pi(\text{reg}) \rightarrow {}^2\Sigma$, due to BH⁺, has been photographed and analyzed.

EXPERIMENTAL DETAILS

The hollow cathode lamp used to excite the spectrum is essentially of the Schüler type,

modified to permit rapid changes of the cathode and to provide forced water circulation around the cathode. A section of the lamp is shown in Fig. 1. To change the cathode one merely removes the glass cap at the left, fastened by picien, unscrews a cylindrical plug, and removes the cathode with a threaded tool. The lamp is much more convenient in surveying the spectra of a series of elements than the older type in which the cathode was pushed in from the window at the right. In this arrangement the cathode frequently stuck after the lamp had been run for some time and had to be drilled out.

The discharge was excited by a Phanotron bridge set at about 1200 volts a.c., 1 to 1.25 amperes. A copper cathode containing powdered boron was used. Helium and hydrogen were circulated through the lamp, and the proportions of the mixture were varied by controlling the cooling of the charcoal and chabuzite traps in the circulation system. When properly adjusted for photographing on the 21-foot grating the Hα line and the nearby He λ6678 were visually about equally intense and the hydrogen many-lines spectrum was faint when viewed in a hand spectroscope.

The discharge was operated at the lowest pressure which would give a steady intense cathode glow. At higher pressures the band spectra became weaker relative to the line spectra appearing.

Curiously, the bands of CuH were not excited

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[1] W. Lochte-Holtgreven and E. S. van der Vleugel, Zeits. f. Physik 70, 188 (1931).

[2] R. F. Paton and G. M. Almy, Phys. Rev. 37, 1710 (1931).

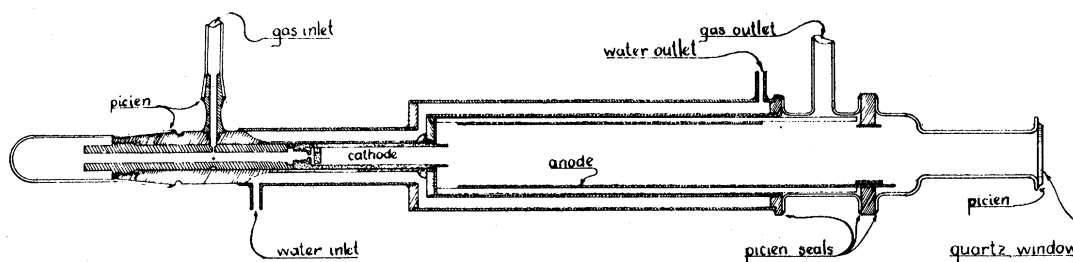[3] S. F. Thunberg, Zeits. f. Physik 100, 471 (1936).

Fig. 1. Section of hollow cathode lamp.

nor do the hydrides of the somewhat similar metals Au and Na appear when these are placed in the cathode. The spectra of the hydrides of the alkaline earths, and of Zn, Cd and Hg, can be obtained with great intensity, as can those of Al and B.

The plates used in the analysis were obtained in the first order of a 21-foot, 30,000-lines-per-inch grating, with an iron arc providing the standard wave-lengths. For interpolating wave numbers directly use was made of the practical formula,

$$v = A/(B+x), \qquad (1)$$

where A and B are constants and x is the distance along the plate from an arbitrary reference point. This approximate formula follows from the general grating equation,

$$v = \frac{n/d}{\sin i + \sin \theta}. \qquad (2)$$

$\theta = (D+x)/R$, where D is the distance along the arc from the center of curvature of the grating to the reference point from which x is measured and R is the radius of curvature of the grating. Substitute for θ in Eq. (2), expand sin $(D+x)/R$, make the approximation, sin $(x/R) = x/R$ and lump constants to obtain Eq. (1). A correction curve is necessary. This formula is especially useful when a computing machine with automatic division is available.

$^1\Pi \rightarrow {}^1\Sigma$ BAND SYSTEM OF B^{11}H

Our determinations of the wave numbers of the (0,0) and (1,1) $^1\Pi \rightarrow {}^1\Sigma$ bands of B^{11}H agree well with those of Thunberg and will not be recorded here. The wave numbers and quantum assignments of the new (2,2) band are given in Table I. We agree that Thunberg's revised

numbering of the (0,0) Q branch follows from a consideration of the Λ type doubling, especially from a comparison of this effect in the three bands. The rotational constants of the three bands, obtained by a graphical method, are given in Table II. Thunberg's B_e and α_e of the $^1\Pi$ state need revision because B_v is not a linear function of $(v+\frac{1}{2})$; γ in the table is the constant appearing in $B_v = B_e - \alpha(v+\frac{1}{2}) + \gamma(v+\frac{1}{2})^2$. Otherwise our values of the rotational constants agree with his, generally within the probable errors of calculation (about ± 0.002 for any B_v).

Each of the three bands shows an abnormally sharp drop in intensity of rotational lines, the decrease occurring near $K' = 26$ in the (0,0) band, $K' = 21$ in the (1,1) band, $K' = 14$ in the (2,2) band. The visual estimates of intensity for (2,2) are given in Table I. These observations, combined with the fact that the (3,3) band is not observed on plates on which the (2,2) band is strong, show fairly conclusively that either

TABLE I. Wave numbers, quantum assignments and intensities (eye-estimates) of the (2,2) band of the $^1\Pi \rightarrow {}^1\Sigma$ system of B^{11}H.

K''	P	Int.	Q	Int.	R	Int.
0					22569.70	2
1			22547.79	5	588.64	2
2	22503.77	0	544.51	5	605.92	2
3	478.87	1	539.74	6	621.51*	6
4	452.57	3	533.30	6	635.35	4
5	424.68	3	525.07	6	647.21	3
6	395.13	4	514.96	6	656.83*	4
7	363.99	2	502.91	6	664.27	2
8	331.09	3	488.63	5	669.12	3
9	296.27	2	472.04	5	671.20	3
10	259.38	2	452.77	5	670.07	3
11	220.21	3	430.65	4	665.52	4
12	178.48	2	405.30	4	656.83*	4
13	133.88	2	376.32	2	643.79	4
14	085.83	od	343.90	1	missing	
15	missing		atomic line	10		
16			missing			

* Indicates superposition.

predissociation or dissociation by rotation takes place in the $^1\Pi$ state. As in the case of the analogous AlH bands, it is undoubtedly the latter. Lochte-Holtgreven and van der Vleugel remarked that at high pressures the lines of higher rotational quantum number in the (0,0) and (1,1) bands became diffuse, which is to be expected when dissociation by rotation is possible.

Since only the diagonal bands $(v' = v'')$ are obtained on even the most intense photographs, the individual vibrational constants of the two states cannot be obtained. With three diagonal bands one can obtain the coefficients of the equation,

$$v_0(v, v) = v_e + (\omega_e' - \omega_e'')(v + \tfrac{1}{2})$$
$$- (x_e'\omega_e' - x_e''\omega_e'')(v + \tfrac{1}{2})^2. \quad (3)$$

The origins, $v_0(v, v)$, were calculated from the frequencies of the first few lines in the P and R branches and the rotational constants of Table II with the results,

$$v_0(0,0) = 23{,}074.0 \text{ cm}^{-1},$$
$$v_0(1,1) = 22{,}891.8 \text{ cm}^{-1},$$
$$v_0(2,2) = 22{,}549.2 \text{ cm}^{-1}.$$

Substituting these in Eq. (3) one obtains on solving,

$$v_e = 23{,}104.0 \text{ cm}^{-1},$$
$$\omega_e' - \omega_e'' = -21.8 \text{ cm}^{-1},$$
$$x_e'\omega_e' - x_e''\omega_e'' = 80.2 \text{ cm}^{-1}.$$

We may assume that both molecular states arise from a combination of normal $2p\,^2P$ boron and normal ^2S hydrogen atoms.[4] The lower, $^1\Sigma$

TABLE II. *Rotational constants of singlet states of $B^{11}H$ (in cm^{-1}).*

CONSTANT	$^1\Sigma$	$^1\Pi$
B_0	11.812	11.918
B_1	11.399	11.187
B_2	10.989	10.246
α_e	0.412	0.521
γ_e		−0.105
B_e	12.018	12.152
D_0	−0.00122	−0.00141
D_1	−0.00118	−0.00165
D_2	−0.00114	−0.00211
D_e	−0.00124	−0.0013
r_e	1.225A	1.219A

[4] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932). The present argument with regard to the triplet states is not given explicitly by Mulliken but is implied in his Fig. 35 which shows the observed and predicted states of BH, and in his discussion of similar examples.

state is tightly bound and, by analogy with AlH, may be expected to show a normal relationship among constants. In particular, from $\omega_e''^2 = 4B_e''^3/D_e''$, we find $\omega_e'' = 2366$ cm^{-1}; in AlH ω_e'', similarly calculated, agrees excellently with ω_e'' obtained from vibrational analysis, well within the uncertainty due to error in D_e''.[5] Since $\omega_e' - \omega_e'' = 21.8$ cm^{-1}, $\omega_e' = 2344$ cm^{-1}. This is a more reliable value than $[4B_e'^3/D_e']^{\frac{1}{2}}$, which gives 2300 cm^{-1}, since the upper state is shallow and D_e' less certainly known than D_e''.

To estimate $x_e'\omega_e'$ and $x_e''\omega_e''$ Thunberg uses the semiempirical relation $x_e = 0.6\alpha_e/B_e$ and obtains $x_e''\omega_e'' = 49$ cm^{-1}, $x_e'\omega_e' = 85$. Our value of $x_e''\omega_e''$ is on this basis about the same. We will accept it as the best available value. Then our relatively exact determination of $x_e'\omega_e' - x_e''\omega_e''$ requires that $x_e'\omega_e' = 129$ cm^{-1}. Hence the best available constants are:

$$\omega_e'' = 2366 \text{ cm}^{-1}, \qquad \omega_e' = 2344 \text{ cm}^{-1},$$
$$x_e'\omega_e' = 49 \text{ cm}^{-1}, \qquad x_e'\omega_e' = 129 \text{ cm}^{-1}.$$

We may now fix limits for the heat of dissociation (also denoted by D_e) of both singlet states of BH. For $^1\Pi$ D_e' certainly lies between the energies of the states $v' = 2$, $K' = 0$ and $v' = 2$, $K' = 14$. That is to say, 0.63 e.v. $< D_e' < 0.88$ e.v. The upper limit is further reduced if one admits that the absence of the (3,3) band is due to the instability of the state $v' = 3$, $K' = 0$; then, $D_e' < 0.82$ volt. We conclude that $D_e' = 0.73$ volt with a probable error of about 0.05 volt. It follows that for the $^1\Sigma$ ground state,

$$D_e'' = v_e + D_e' = 3.60 \pm 0.05 \text{ volts.}$$

An alternative method of calculating the heat of dissociation is to use the relation $D_e'' = \omega_e''^2/4x_e''\omega_e''$. This gives $D_e'' = 3.5$ volts. Since the reliability of this method is much inferior to that making use of dissociation by rotation the agreement is to be taken as an indication of the accuracy of $x_e''\omega_e''$, obtained with the use of $x_e'' = 0.6\alpha_e''/B_e''$.

$^3\Sigma \rightarrow ^3\Pi$ BAND SYSTEM OF $B^{11}H$

Lochte-Holtgreven and van der Vleugel[1] discovered a band system with (0,0) head at 3694A whose general appearance and rotational

[5] W. Holst and E. Hulthén, Zeits. f. Physik **90**, 712 (1934).

constants are similar to those of the singlet bands. A few lines in the R branch of the (0,0) band were resolved into triplets. Because the two systems were so similar they attributed the triplets to a $^3\Pi \rightarrow {}^3\Sigma$ transition "corresponding" to the $^1\Pi \rightarrow {}^1\Sigma$ transition and, indeed, these are the four states that can arise from normal B and normal H. Since on our plates several lines of the P and R branches are resolved into triplets (Q branch appears as doublets) it is possible to determine the nature of the transition more accurately than has been done. The conclusion, that it is $^3\Sigma \rightarrow {}^3\Pi$, rather than $^3\Pi \rightarrow {}^3\Sigma$, is supported by theoretical considerations which will be discussed.

The wave numbers and quantum assignments appear in Table III. The combination differences,

$$\Delta_2 F_i{}'(K) = R_i(K) - P_i(K),$$
$$\Delta_2 F_i{}''(K) = R_i(K-1) - P_i(K+1),$$

where $i = 1$, 2, 3 were computed. The spin splitting in both states is evidently small and the states near case b. Since for singlet or pure case b states,

$$\Delta_2 F(K) = 4B(K+\tfrac{1}{2}) + 8D(K+\tfrac{1}{2})^3 + \cdots , \quad (4)$$

we have plotted in Fig. 2, $\Delta_2 F(K)/4(K+\tfrac{1}{2})$ against $(K+\tfrac{1}{2})^2$ for the six substates. For a $^3\Sigma$ state the effect of the splitting should be very small for low K and the plots for the three substates should coincide. For a $^3\Pi$ state not pure case b the lines should diverge as K de-

creases, on account of rotational distortion. It is clear that there is coincidence in the upper state but a definite divergence in the lower, indicating that the transition is $^3\Sigma \rightarrow {}^3\Pi$.

Next we may consider the relation of the molecular states of BH to the atomic states of the separated atoms and of the "united atom," carbon.[4] The normal atomic states, $2s^2 2p\,{}^2P$ of B and $1s\,{}^2S$ of H give four molecular states $^1\Sigma^+$, $^1\Pi$, $^3\Sigma^+$, $^3\Pi$. The united atom, carbon, has three low atomic states from the configuration $2s^2 2p^2$, namely, ^3P (normal), ^1D, ^1S, which give, on separating the atom, the following molecular states:

$$^3\Pi \text{ and } {}^3\Sigma^- \text{ from } {}^3P,$$
$$^1\Delta, \ {}^1\Pi, \ {}^1\Sigma^+ \text{ from } {}^1D,$$
$$^1\Sigma^+ \text{ from } {}^1S.$$

In this group there is no $^3\Sigma^+$; the lowest $^3\Sigma^+$ comes from $2s^2 2p3s\,{}^3P$, 7.4 volts above the ground ^3P. $^3\Sigma^+$ from normal B and normal H is therefore repulsive or, at the least, less attractive than the $^3\Pi$ which goes into normal ^3P on pushing B and H together. On the other hand, $^3\Sigma^-$ from normal ^3P of C cannot dissociate into any observed state of B and normal H. However, the first excited state of B, $2s^2 3s\,{}^2S$(at 4.95 volts) would give $^3\Sigma^+$ with normal H. This is most probably the upper state of the triplet system. In this case it is about 1.6 volts more tightly bound than the lower $^3\Pi$ state since the corresponding atomic transition (4.95 volts) is

TABLE III. *Wave numbers and quantum assignments of* $^3\Sigma \rightarrow {}^3\Pi$ *system of* $B^{11}H$. *Subscript 3 corresponds to* $^3\Pi_2$, $J'' = K'' - 1$; *2 to* $^3\Pi_1$, $J'' = K''$; *1 to* $^3\Pi_0$, $J'' = K'' + 1$.

K''	P_3	P_2	P_1	R_3	R_2	R_1	Q_3	Q_2	Q_1
2	27010.08	27007.96	27006.39	27131.19	27129.39	27127.51	27057.98	27056.22?	27054.66
3	26981.96	26980.64	26979.21	151.51	149.62	148.50	054.66	053.34	051.48
4	952.98	951.95	950.94	170.35	169.29	168.33	unresolved	048.72	047.17
5	923.31	922.36	921.69	188.38	187.63	186.78	"	042.94	041.71
6	892.81	892.09	891.43	205.29	204.58	203.80	"	036.07	034.90
7		860.48		220.74	220.17	219.48	"	028.03	026.95
8	829.04	828.51	828.02	235.12	234.48	233.92	"	018.85	017.90
9	795.85	795.49	795.03	unresolved	247.44	"	"	008.56	007.62
10	761.98	761.45	760.87	"	258.86	"	"	26997.11	26996.17
11	unresolved	726.57	unresolved	"	268.65	"	"	984.44	983.59
12	691.26	690.94	690.57	"	277.37	"	"	970.63	969.75
13	654.83	654.47	654.07	"	284.15	"	"	955.73	954.77
14	617.56	617.21	616.82	"	290.14	"	"	939.55	938.62
15	579.41	579.11	578.88	"	294.65	"	"	922.08	unresolved
16	540.69	540.42	540.07	"	297.02 (head)	"	"	903.36	"
17	unresolved	500.39	unresolved				"	883.47	"
18	"	460.63	"				"	862.65	"
19	"	419.66	"				"	840.81	"
20	"	377.91	"						

about 1.6 volts greater than the molecular electronic energy change.

Holst has observed the apparently analogous triplet system in AlH.[6]

The rotational constants of the $^3\Sigma$ state have been obtained graphically from Fig. 2. Eq. (4) applies and shows that the slope of the coincident lines for the three Σ states is $2D_0'$ and that the intercept at $(K+\frac{1}{2})^2=0$ is B_0'. The constants B_0 and D_0 for the $^3\Pi$ state have been determined by Challacombe and Almy[7] using Gilbert's method.[8] The electronic coupling constant λ, or A/B, has also been determined by Gilbert's method and verified by a graphical method suggested by Budo's treatment[9] of the Hill and Van Vleck theory for $^3\Pi$ states. The results are,

$$B_0''= 12.667, \qquad B_0'= 12.126,$$
$$D_0''= -0.00122, \qquad D_0'= -0.00128,$$
$$r_0''= 1.198A, \qquad r_0'= 1.220A,$$
$$\lambda= +0.47,$$

The $^3\Pi$ state is regular and near case b.

The Λ type doubling for each of the three sub-levels of the Π state is shown in Table IV and Fig. 3. For pure case b the splitting should be the same in each sublevel and proportional to $K(K+1)$.[10] From the graph it appears that there is some departure from pure case b Λ type doubling. Following Hebb's treatment of this effect in $^3\Pi$ state, one might make a detailed comparison with theory, but this has not been done. The cd designation is based upon the assumption that the upper state is $^3\Sigma^+$.

$^2\Pi \rightarrow {}^2\Sigma^+$ BAND SYSTEM OF $B^{11}H^+$

With the hollow cathode source a band appears with R head at 3766A, approximately as intense as the triplet band discussed above. A weaker head appears at 3803A. These two heads are assumed to be the (0,0) and (1,1) bands of a system. Only the (0,0) band has been measured and analyzed.

The (0,0) band exhibits P, Q and R branches, each branch consisting of narrow doublets whose interval converges as K increases. The wave numbers and quantum assignments appear in Table V. The general features of the system
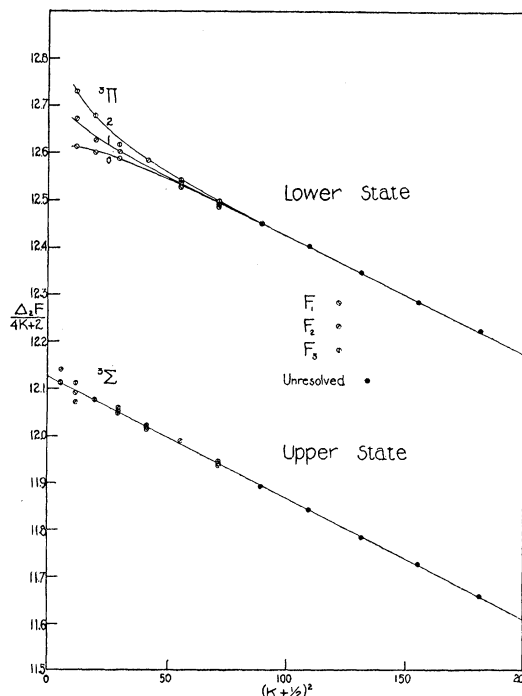
[6] W. Holst, Zeits. f. Physik 86, 338 (1934).
[7] To be published soon.
[8] Cecil Gilbert, Phys. Rev. 49, 619 (1936).
[9] A. Budo, Zeits. f. Physik 96, 219 (1935).
[10] M. H. Hebb, Phys. Rev. 49, 610 (1936).

FIG. 2. $\Delta_2F(K)/4K+2$ for each triplet substate.

indicate a transition between a Π and a Σ state and a detailed consideration of missing lines shows that it fits the assignment $^2\Pi(\text{reg}) \rightarrow {}^2\Sigma$ with a $^2\Pi$ state whose coupling is intermediate between the two pure case b conditions ($\lambda = 0$ and $\lambda = 4$). That is to say, the P_1, Q_1, R_1 branches lie to the violet from the P_2, Q_2, R_2 branches, respectively, or, $F_1(K)$ of $^2\Pi$ lie above $F_2(K)$. If λ is less than 0 or greater than $+4$, $F_2(K)$ lies above $F_1(K)$. To see that the missing lines near the origin are just those one would expect to be missing one may compare Table V with Jevons' *Report on Band Spectra of Diatomic Molecules*, Fig. 40(i).

That the transition is $^2\Pi \rightarrow {}^2\Sigma$ is supported by the behavior of the values of Δ_2F for the two states. For the lower state these differences are identical within errors of observation for the F_1 and F_2 levels. This is characteristic of a $^2\Sigma$ state with negligible doubling. In the upper state Δ_2F_2 and Δ_2F_1 diverge as K decreases as when rotational distortion is occurring. Rather fragmentary observations on the isotopic spectrum accompanying the system support the assumption that the molecule is boron hydride. This BH^+ system corresponds to the well-known
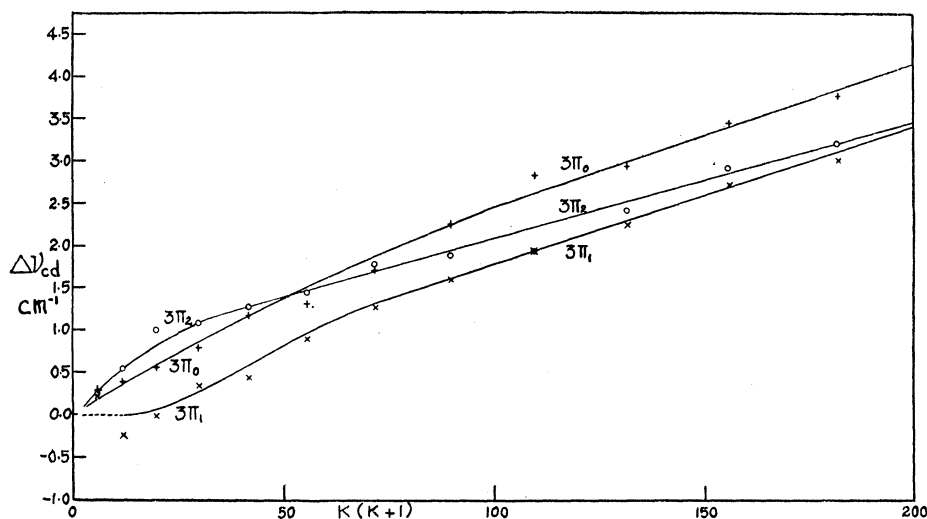
FIG. 3. Λ type doubling of $^3\Pi$ substates.

$^2\Pi\rightarrow{}^2\Sigma$ green BeH bands and to the AlH$^+$ bands.

Before calculating the rotational and electronic coupling constants of BH$^+$ we will refine the theory of $^2\Pi$ states somewhat beyond the stage discussed by Hill and Van Vleck.[11] In a recent paper Gilbert[8] has shown how the theory of Van Vleck for $^3\Pi$ states intermediate between case a and case b may be modified to take better account of the rotational D term. In the improved theory the D term is not considered merely as a fixed term to be added to each component of a molecular multiplet ($DK^2(K+1)^2$ near case b or $DJ^2(J+1)^2$ near case a) but is included in the Hamiltonian function of the unperturbed (case a) system. It is then shown that the D term is not the same for all components of a multiplet. Gilbert gives a neat method for finding the rotational and electronic coupling constants of triplet states under the refined theory. The corresponding theory for doublet states can be written down at once.

THEORY OF $^2\Pi$ STATES

The Hamiltonian for case a used by Gilbert is,

$$H_a = H + \mu H^2 + \lambda\Lambda\Sigma,$$

where $\mu = D/B$, $\lambda = A/B$. $H+\lambda\Lambda\Sigma$ is the matrix for case a given by Van Vleck, μH^2 is the new term including the effect of the D term. As in

11 E. L. Hill and J. H. Van Vleck, Phys. Rev. 32, 250 (1928).

Gilbert's paper, Van Vleck's matrices will be divided by B. The elements of $H_a(\Sigma, \Sigma')$ are

$$\left\|
\begin{array}{c}
(J^*-7/4)+\mu[(J^*-7/4)^2+(J^*-\tfrac{3}{4})]+\lambda/2 \\
(J^*-\tfrac{3}{4})^{\frac12}[1+2\mu(J^*-\tfrac{3}{4})] \\
(J^*-\tfrac{3}{4})^{\frac12}[1+2\mu(J^*-\tfrac{3}{4})] \\
(J^*+\tfrac{1}{4})+\mu[(J^*+\tfrac{1}{4})^2+(J^*-\tfrac{3}{4})]-\lambda/2
\end{array}
\right\|,$$

where $J^* = J(J+1)$.

The energies are the roots of the equation,

$$\left|
\begin{array}{cc}
\dfrac{F}{B}-H_a(\tfrac{1}{2},\tfrac{1}{2}) & -H_a(+\tfrac{1}{2},-\tfrac{1}{2}) \\[2ex]
-H_a(-\tfrac{1}{2},\tfrac{1}{2}) & \dfrac{F}{B}-H_a(-\tfrac{1}{2},-\tfrac{1}{2})
\end{array}
\right| = 0. \quad (5)$$

TABLE IV. Λ type doubling of $^3\Pi$. Values of $\Delta\nu_{cd}$ are listed where $2\Delta\nu_{cd}(K+\tfrac{1}{2}) = [R(K)-Q(K+1)] - [Q(K)-P(K+1)]$.

$K+\tfrac{1}{2}$	$^3\Pi_2$	$^3\Pi_1$	$^3\Pi_0$
$2\tfrac{1}{2}$	0.25	0.23	0.29
$3\tfrac{1}{2}$	0.55	−0.23	0.40
$4\tfrac{1}{2}$	1.00	0.00	0.57
$5\tfrac{1}{2}$	1.09	0.36	0.80
$6\tfrac{1}{2}$	1.28	0.45	1.18
$7\tfrac{1}{2}$	1.45	0.90	1.32
$8\tfrac{1}{2}$	1.78	1.28	1.71
$9\tfrac{1}{2}$	1.88	1.61	2.26
$10\tfrac{1}{2}$	1.94	1.94	2.84
$11\tfrac{1}{2}$	2.42	2.26	2.95
$12\tfrac{1}{2}$	2.92	2.74	3.46
$13\tfrac{1}{2}$	3.22	3.04	3.79
$14\tfrac{1}{2}$	3.96	3.81	4.16
$15\tfrac{1}{2}$	4.95	4.81	4.64
$16\tfrac{1}{2}$	5.29	5.29	5.29

If we let

$$E = \frac{F}{B} - \tfrac{1}{2}[H_a(\tfrac{1}{2}, \tfrac{1}{2}) + H_a(-\tfrac{1}{2}, -\tfrac{1}{2})], \quad (6)$$

the determinant Eq. (5) becomes, on expanding.

$$E^2 = \tfrac{1}{4}[H_a(\tfrac{1}{2}, \tfrac{1}{2}) - H_a(-\tfrac{1}{2}, -\tfrac{1}{2})]^2$$

$$+ H_a^2(\tfrac{1}{2}, -\tfrac{1}{2}) = \alpha. \quad (7)$$

Then $E = \pm\sqrt{\alpha}$ are the solutions, where

$$\alpha = \frac{(\lambda - 2)^2}{4} + \frac{4J^* - 3}{4}\left[1 + \mu(4J^* + 1 - 2\lambda)\right.$$

$$\left. + \mu^2\left(\frac{4J^* - 1}{2}\right)^2 - \mu^2\right]. \quad (8)$$

Finally, from Eq. (6),

$$F(J) = B(J^* - \tfrac{3}{4}) + D\left(J^{*2} - \frac{J^*}{2} + \frac{13}{16}\right) \pm B\sqrt{\alpha}. \quad (9)$$

These are the energies of the states for a particular value of J. The upper $(+)$ sign goes with $J = K - \tfrac{1}{2}$, or F_2 levels. The lower $(-)$ sign, goes with $J = K + \tfrac{1}{2}$, or F_1 levels. If terms in D are dropped the expression for $F(J)$ reduces to the

Hill and Van Vleck formula. If another rotational term is needed FJ^{*3} (not the above F) may be added to each component just as D and F terms have been added in using the Hill and Van Vleck theory.

Calculation of B and D

We may write,

$$\text{Spur } F(J) = B \text{ Spur } H_a$$

$$= B[H_a(\tfrac{1}{2}, \tfrac{1}{2}) + H_a(-\tfrac{1}{2}, -\tfrac{1}{2})]$$

$$= -(3/2)B + (13/8)D$$

$$+ (2B - D)J^* + 2DJ^{*2}.$$

Hence

$$\Sigma\Delta_2 F(J) = \Delta_2 F_1(J) + \Delta_2 F_2(J)$$

$$= \text{Spur } F(J+1) - \text{Spur } F(J-1)$$

$$= 8(B + D)(J + \tfrac{1}{2}) + 16D(J + \tfrac{1}{2})^3. \quad (10)$$

Thus if one plots the mean $\Delta_2 F(J)$ divided by $4J + 2$ against $(J + \tfrac{1}{2})^2$ one should obtain a straight line of slope $2D$, intercept, $B + D$. If the line is not straight a correction term $24F(J + \tfrac{1}{2})^5$ may be added to Eq. (10).

Fortunately this result is, except for the negligible term $8D(J + \tfrac{1}{2})$ in Eq. (10), exactly the same as in the procedure which has usually been followed in applying the Hill and Van Vleck theory.

TABLE V. *Wave numbers and quantum assignments of (0,0) band of $^2\Pi \rightarrow {}^2\Sigma^+$ system of $B^{11}H^+$. Subscript 1 corresponds to $^2\Pi_{\frac{1}{2}}$, $J' = K' + \tfrac{1}{2}$; subscript 2 to $^2\Pi_{\frac{3}{2}}$, $J' = K' - \tfrac{1}{2}$.*

| K''	P_1	P_2	Q_1	Q_2	R_1	R_2
0			26368.18		26389.87	
1	26335.39		365.59		410.91	26406.78
2	316.52		361.40	26357.17	430.32	427.55
3	287.48	26283.73	356.14	353.28	448.34	446.32
4	257.71	254.77	349.42	347.17	464.71	463.08
5	226.56	224.50	341.20	339.48	479.45	478.15
6	194.29	192.62	331.34	330.03	492.42	491.34
7	160.46	159.18	319.94	318.80	503.48	502.62
8	125.38	124.33	306.98	305.95	512.85	512.12
9	088.85	088.09	292.38	291.50	520.30	519.61
10	051.18	050.50	276.11	275.48	525.91	525.42
11	012.11	011.54	258.33	257.71	529.59	529.17
12	25971.81	25971.35	238.82	238.33	531.50	530.76
13	930.29	929.86	217.84	217.42	531.00	unresolved
14	887.64	887.19	195.06	194.71	528.65	"
15	843.42	unresolved	170.58	unresolved	524.37	"
16	798.11	"	144.64	"	518.05	"
17	751.69	"	117.12	"	509.58	"
18	704.21	"	088.09	"	499.06	"
19	655.54	"	057.07	"	486.38	"
20	605.81	"	024.63	"	471.42	"
21	554.92	"	25990.61	"	454.49	"
22	503.04	"	955.03	"	435.46	"
23	450.08	"	917.84	"	414.26	"
24	396.27		879.44	"	390.35	
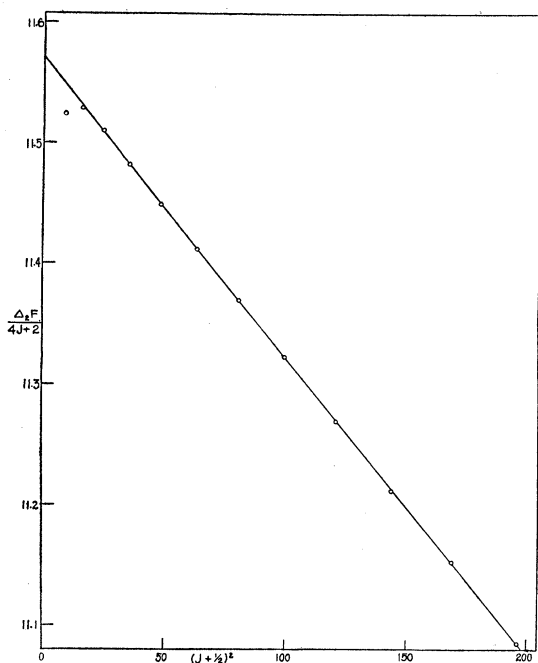
FIG. 4. Mean $\Delta_2 F/4J+2$ for $^2\Pi$ state. The slope is $2D_0$, the intercept $B_0+D_0+\frac{1}{2}q^*$.

We have not, however, considered the effect of Λ type doubling on this calculation. Mulliken and Christy[12] have given a complete expression for the energy of a $^2\Pi$ state with terms for Λ type doubling included (but without D terms). Their equation stands, with the present modification of theory, if the D term of Eq. (9) is added and if $\sqrt{\alpha}$ is substituted for their $X/2$. An examination of their equation shows that if one takes the mean of all four values of $\Delta_2 F(J)$, that is, for $1c$, $1d$, $2c$, $2d$ sublevels, the Λ doubling correction terms subtract off except for a term $\frac{1}{2}q^*(J+\frac{1}{2})$. This term may be considered as a correction on the term in $(J+\frac{1}{2})$ in Eq. (10) so that in the method for evaluating B and D, the intercept is not $B+D$ but $B+D+\frac{1}{2}q^*$. q^* can be determined from a study of the Λ type doubling. Near case b, as in BH^+, it may be taken as the experimentally determined coefficient q_0 in Eq. (13).

Calculation of λ

One may obtain λ from the relation,

$$F_2(J) - F_1(J) = 2B\sqrt{\alpha}.$$

[12] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

α depends upon J (Eq. (8)). One substitutes the observed J doublet intervals on the left and solves for $(\lambda-2)^2$, and hence λ, for various values of J. The ambiguity in λ must be removed by a consideration of missing lines, or of Λ type doubling.

The objection to this method is that it deals with a J doublet for which the interval, especially near case b, is due largely to difference of rotational energy. Hence B and D must be precisely known. Near case a the method should work well but near case b it is better to use K doublets. The width of a K doublet is:

$$\Delta\nu_{12}(K) = F_1(K) - F_2(K)$$
$$= B[2K+1+4\mu(K+\tfrac{1}{2})^3$$
$$-(\sqrt{\alpha_1}+\sqrt{\alpha_2})], \quad (11)$$

in which α_1 is α with $J=K-\frac{1}{2}$, α_2 is α with $J=K+\frac{1}{2}$. A term $(\mu/2)(K+\frac{1}{2})$ has been dropped. Solving for $(\lambda-2)^2$,

$$(\lambda-2)^2 = \frac{[(g(K)-\Delta\nu_{12}/B)^2-f(K)}{-f(K+1)]^2-4f(K)f(K+1)}{(g(K)-\Delta\nu_{12}/B)^2}, \quad (12)$$

in which $g(K) = 2K+1+4\mu(K+\tfrac{1}{2})^2$
$$f(K) = (K^2-1)[1-2\mu\lambda-\mu^2$$
$$+4(\mu-\mu^2)K^2+4\mu^2K^4].$$

Calculation of band origin

Writing the equations for the frequencies of the Q_1 and Q_2 lines and adding, one may readily show that,

$$\nu_{00} = \frac{Q_2(J)+Q_1(J)}{2}$$
$$-(B'-B'')J(J+1)+\tfrac{3}{4}B'+\tfrac{1}{4}B''.$$

MOLECULAR CONSTANTS OF BH^+

The rotational constants of the $^2\Pi$ state of BH^+ have been determined graphically in Fig. 4 by the method described, using Eq. (10), and taking into account Λ doubling. The constants for the $^2\Sigma$ state have been obtained by least squares solution for the coefficients in

$$\Delta_2 F(K)/(4K+2) = B+2D(K+\tfrac{1}{2})^2+3F(K+\tfrac{1}{2})^4.$$

Within errors of observation, $\Delta_2 F_1''$ and $\Delta_2 F_2''$

are equal. The results,

$$B_0'' = 12.374, \qquad B_0' = 11.565,$$
$$D_0'' = -0.00125, \qquad D_0' = -0.00124,$$
$$F_0'' = 6.9 \times 10^{-8},$$
$$r_0'' = 1.208\text{A}, \qquad r_0' = 1.248\text{A}.$$
$$v_{00} = 26376.2 \text{ cm}^{-1},$$

The coupling constant λ for the $^2\Pi$ state of BH$^+$ has been determined by applying Eq. (12) to each observed K doublet between $K=2$ and $K=11$. The data were obtained from a careful measurement of the Q branch on a rather faint second order plate. Thus intervals between c levels are used. Since, as is shown below, the Λ doubling is practically the same for the F_1 and F_2 levels, the results would not be appreciably changed if the d levels were used. The results are shown in Fig. 5. A constant value of λ is not obtained. The main reason for refining the theory was to see if one might thereby get a more consistent value of λ than is obtained with the Hill and Van Vleck theory (dotted line in Fig. 5). The situation is not much improved. The remaining discrepancy is presumably due to doubling in the $^2\Sigma$ state. Theoretically if there is a "pure precession" relation between a $^2\Pi$ and a $^2\Sigma$ state, the doubling in the $^2\Sigma$ state is $\Delta v_{12}(K)$ $= \gamma(K+\frac{1}{2})$ where $\gamma = \lambda q_0$ and q_0 is a coefficient in the expression for Λ doubling in the $^2\Pi$ state (Eq. (13)). In the case of BH$^+$ the electron configurations are $2s\sigma^2\ 2p\pi$ and $2s\sigma^2\ 2p\sigma$ and one may expect approximately pure precession.[12] We find experimentally (below) that $q_0 = 0.016$ and hence $\gamma = 0.02$. Since the observed spin doubling is $\Delta v_{12}(^2\Pi) - \Delta v_{12}(^2\Sigma)$ the observed intervals should be increased by $0.02(K+\frac{1}{2})$ before λ is evaluated. This change would, as a matter of fact, give a fairly constant λ, though the correction overshoots somewhat (at $K=10$, the corrected λ is 1.30). In the absence of satellite branches, γ can only be determined experimentally from a study of $\Delta_2 F(K)$, since $\Delta_2 F_1(K)$ $- \Delta_2 F_2(K) = 2\gamma$. For BH$^+$ 2γ is 0.04 cm^{-1}. The data on BH$^+$ are not sufficiently precise to enable an estimate to be made in this way. Since the uncertainty in the $^2\Pi$ doublet interval is least for low K, the best value of λ is obtained in this range. We conclude from Fig. 5 that

$$\lambda = 1.21 \pm 0.01, \qquad A = \lambda B = 14.0 \text{ cm}^{-1}.$$
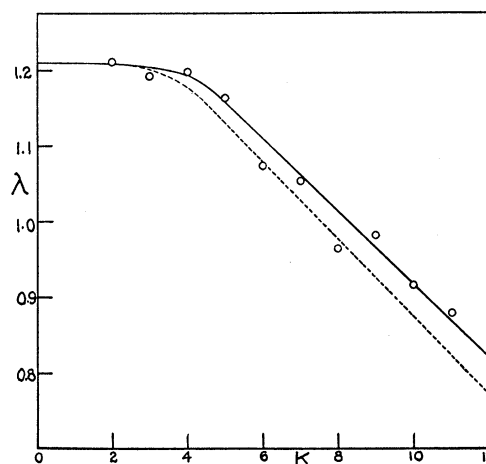

FIG. 5. Values of electronic coupling constant (λ) obtained with Eq. (12) (solid line) and from Hill and Van Vleck theory (dashed line). The plotted points go with the solid line.

In the case of the analogous $^2\Pi$ state of the isoelectronic molecule BeH, Olsson[13] found that the observed doublet intervals fit the Hill and Van Vleck theory without correction for $^2\Sigma$ splitting. This is to be expected because the $^2\Sigma$ splitting is theoretically much smaller than in BH$^+$, since λ is smaller. That is to say, $\gamma = \lambda q_0$ $= 0.0029$, using the experimental $q_0 = 0.0142$. In the range in which the theory was applied $(K < 11)\Delta v_{12}(^2\Sigma)$ is less than 0.03 cm^{-1} and the correction to the computed λ would be inappreciable.

The Λ type doubling, calculated for each component of the $^2\Pi$ state according to the equation

$$2\Delta v_{dc}(K+\tfrac{1}{2}) = [R(K) - Q(K)]$$
$$- [Q(K+1) - P(K+1)]$$

is plotted in Fig. 6. Van Vleck's theory of Λ type doubling, as formulated and extended by Mulliken and Christy[12] predicts that for either sublevel in case b,

$$\Delta v_{dc}(K) = q_0[(K+\tfrac{1}{2})^2 + (4D/B)(K+\tfrac{1}{2})^4].$$

$$q_0 = \left[\frac{2B_v l(l+1)}{\nu(\Pi, \Sigma)}\right] \quad (13)$$

Negligible terms are dropped. $q_0 = [2B_v^2 1(1+1)/$
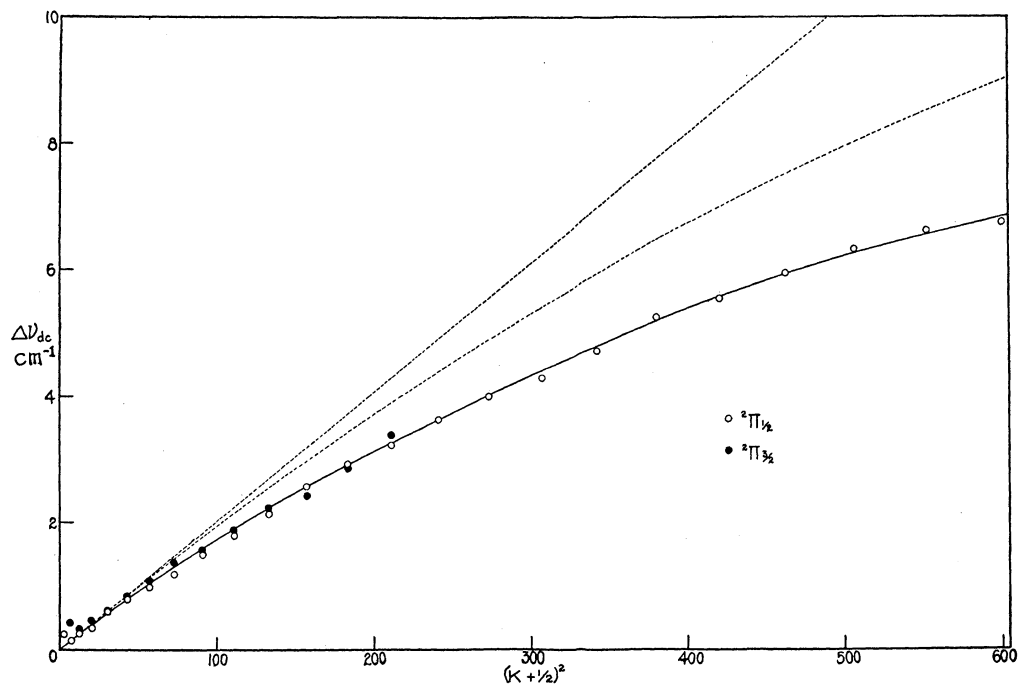
[13] E. Olsson, Zeits. f. Physik 73, 732 (1932).

FIG. 6. A type doubling in $^2\Pi$ state of BH$^+$. Solid curve: $0.0164(K+\frac{1}{2})^2-0.086\times10^{-4}(K+\frac{1}{2})^4$. Upper dashed curve: $q_0(K+\frac{1}{2})^2$. Lower dashed curve: Eq. (13).

$v(\Pi, \Sigma)$], in the case of pure precession. The curve through the plotted points shows that the observed doubling can be fitted accurately by the equation,

$$\Delta v_{dc} = 0.0164(K+\tfrac{1}{2})^2 - 0.086\times10^{-4}(K+\tfrac{1}{2})^4,$$

in which the coefficients were obtained by least squares. The corresponding theoretical coeffi-
cients are $q_0 = 0.0204$ and $4q_0D_0/B_0 = -0.090 \times 10^{-4}$. The curves obtained with the latter coefficients, with and without the fourth power term, are shown. The departure from pure precession and the improvement in the shape of the curve when the fourth-power term (due to stretching with rotation) is added is very like that found in BeH.[12]