Ultraviolet Spectra of BeH and BeH$^+$

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A BeH band system analogous to the $B^2\Pi \rightarrow X^2\Sigma$ MgH system is reported. Observed bands are the (0,0) at 1960A, (1,0) at 1882A and (1,1) at 1956A. Each consists of a single Q branch (negligible spin doubling), P and R branch transitions being eliminated by predissociation from the $^2\Pi$ state into a neighboring unstable $^2\Sigma$ state. For the $^2\Pi$ state $B_0 = 10.65$ cm^{-1} and $\omega_e - 2x_e\omega_e = 2133.4$. The complex BeH spectrum from 3100A to 3600A consists only of an extension of the known $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ BeH$^+$ system. Analyses of the principal BeH$^+$ bands in this region yield revised values for the band constants.

THERE has been but a single band system, a $^2\Pi \rightarrow {}^2\Sigma$ transition with principal head at 5000A, so far reported for the neutral BeH molecule.[1] In addition an extensive system of bands due to BeH$^+$, covering practically all of the quartz ultraviolet region of the spectrum, has been partially analyzed.[2] Since for the corresponding MgH molecule two more electronic transitions are known, it was thought likely that as yet undiscovered BeH systems existed. In particular we have searched for and found in the near vacuum ultraviolet BeH bands analogous to the $B^2\Pi \rightarrow X^2\Sigma$ system of MgH. This new BeH system forms the second member of a Rydberg series, the first member of which is the green $^2\Pi \rightarrow {}^2\Sigma$ system, has its principal head at 1960A and exhibits the same interesting predissociation observed in the MgH bands near 2430A. In fact, although these new BeH bands represent a $^2\Pi \rightarrow {}^2\Sigma$ system, due to this predissociation they possess Q branches only. We give the details below.

In the region 3100A–3600A there is a considerable accumulation of hydride band lines, especially about the $3p\,{}^3P$–$3s\,{}^3S$ multiplet of Be I at 3321A. Although this "many-lined" spectrum was believed to be made up in part of an extension of the known BeH$^+$ system to higher v'' levels, it was suspected that it also contained another BeH system. Our quantum analysis shows, however, that almost all of the lines of appreciable intensity in this region are assignable to BeH$^+$ bands. The great density of band lines is due to the tendency for the spacing of successive bands in sequences $\Delta v = -3$, -4, etc. to be reduced to zero with increasing v. There may be another BeH system composed of fainter lines in this region, but it is not evident.

Recently Guntsch[3] has found a $^2\Sigma^- \rightarrow A^2\Pi$ MgH band at 4400A. The corresponding BeH band would be expected to occur at about 4050A. Near this wave-length on our spectrograms we find many band lines but, owing partly to the presence of band structure of impurities, and partly to the lack of obvious band branches, we have not attempted the analysis.

The spectrograms of the 1960A system were made with a vacuum spectrograph having an aluminized speculum metal grating with a 10-foot radius of curvature and giving a dispersion of 5.5Å per mm. A hollow cathode discharge employing a molybdenum cylinder charged with small pieces of beryllium as a cathode carrying 0.8 ampere either in pure hydrogen or in hydrogen-helium mixtures at about 5 mm pressure produced the 1960A band very well. More intense spectrograms were obtained with a 220-volt d.c. arc between Be electrodes in a hydrogen atmosphere at 5 cm pressure, the light being focused on the slit with a large fluorite lens. A fluorite window covered the slit in all the exposures. The hollow cathode discharge showed also the H_2 continuum as well as the H_2 many-lined spectrum beginning at 1650A. Atomic lines of Be I and Be II together with lines of Al II and Al III always present in our Be spectra served as standards for the wave-length measurement. The BeH$^+$ spectrum in the 3100-3600A range was

[1] For references cf. W. Jevons, *Report on Band Spectra of Diatomic Molecules*.

[2] Cf. 1. Also E. Bengtsson Knave, Dissertation, Uppsala, 1932.

[3] A. Guntsch, Zeits. f. Physik **104**, 584 (1937).

photographed with a dispersion of 1.58A per mm, using the 220-volt d.c. Be arc as a light source.

The 1960A BeH Bands

The principal feature of this new BeH system is a single strong band branch degrading to higher frequencies from a head at 1960A. From the closeness of the rotational line spacing it is to be concluded that the band could only originate in the light BeH molecule providing it represents a Q branch of a transition between two states of nearly the same B_v value. There is no trace of a P branch in the region just to the red of this 1960A head. Now experimentally we find that both Be and hydrogen are necessary to produce the band. Similar hollow cathode discharges in a mixture of H_2 and He but with Al or graphite cathodes or with boron in a molybdenum cathode as well as the Be hollow cathode discharge running in He alone all failed to show the band. The only appreciable impurity lines are those of Al, but on the intense BeH arc exposures the AlH bands at 2033A and 2254A do not appear.

Furthermore, calculation shows that the BeH analog of the $B^2\Pi\rightarrow X^2\Sigma$ 2430A MgH band should occur at approximately this wave-length. The $A^2\Pi\rightarrow X^2\Sigma$ system of MgH has its (0,0) band at 19,271 cm^{-1}, making the interval between the two $^2\Pi$ states 21,966 cm^{-1}. If we assume that the ratio of this interval for MgH to that for BeH is the same as that of the ionization potentials of the two molecules and use for the I.P. the value for the united atom in each case, we calculate the $B^2\Pi-A^2\Pi$ interval for BeH to be 30,516 cm^{-1}. This places the $B^2\Pi\rightarrow X^2\Sigma$ (0,0) band of BeH at 50,547 cm^{-1}, or very close to the frequency 50,980 at 1960A. A rough Rydberg series calculation with the $A^2\Pi\rightarrow X^2\Sigma$ system at 20,031 cm^{-1} as the first member and with the limit placed at the I.P. of the united atom (B, I.P. = 67,068 cm^{-1}) indicates that the second member should be found at 49,924 cm^{-1}, again fairly near to the frequency of the observed band.

We therefore take this 1960A band to be indeed the second member of a Rydberg series of $^2\Pi\rightarrow^2\Sigma$ bands for BeH. In the corresponding MgH system, the P and R branches of the (0,0) and (0,1) bands end abruptly at $J=11$ while the Q branches proceed normally to higher J values.[4] The (1,1) and (1,0) bands possess Q branches only. This sudden cessation of P and R branch transitions has been attributed[5] to the fact that radiationless transitions occur from these particular upper levels to the continuum of a $^2\Sigma^+$ state. In BeH the continuum of this interacting $^2\Sigma^+$ state must begin below the level $J=1$, $v=0$ of the $B^2\Pi$ state, for no P and R branches at all are to be found.

In Table I we list the frequencies and quantum assignments of the lines in this Q branch of the (0,0) $B^2\Pi\rightarrow X^2\Sigma$ band. The J numbering has been made by extrapolating through the region of unresolved lines near the head with the aid of the average second difference between successive lines. Since the spin doubling is negligible in both states, we may apply the formula for the Q-branch frequencies of a $^1\Pi\rightarrow^1\Sigma$ band to obtain values of $B'-B''$ from frequency differences between lines of known J values. By an averaging process, using lines with $J<20$, we compute $B_0'-B_0''=0.4882$. Since $B_0''=10.1622$,[6] $B_0'=10.65$ cm^{-1}. The accuracy of measurement is insufficient for the determination of D_0'.

The (1,0) and (1,1) bands are definitely present but with low intensity in the spectrum of the Be arc. Again only the Q branches occur, the (1,0) head coming at 1882.75A or 2133.4 cm^{-1} from the (0,0) head. It should be noted that this value of $\Delta G(\frac{1}{2})$ is almost as large as that for the ground state of BeH^+, 2140.4 cm^{-1}, whereas the value for the $A^2\Pi$ state is 2007.9 cm^{-1}. The (1,1) head

Table I. *Frequencies and quantum assignments of the lines of the Q branch of the* (0,0) $B^2\Pi\rightarrow X^2\Sigma$ *BeH band at 1960A.*

J	ν	J	ν
1	50,980.4	22	51,226.1
⋮	⋮	23	45.8
6	50,997.8	24	67.1
7	51,005.3	25	92.8
8	13.1	26	316.8
9	21.2	27	39.7
10	31.9	28	67.9
11	42.5	29	93.3
12	54.3	30	416.8
13	66.5	31	47.5
14	78.8	32	74.8
15	94.7	33	500.7
16	109.6	34	29.4
17	27.4	35	57.8
18	45.4	36	92.7
19	64.0	37	
20	83.0	38	657.2
21	202.8		

[4] R. W. B. Pearse, Proc. Roy. Soc. **122**, 442 (1929).

[5] R. deL. Kronig, Zeits. f. Physik **62**, 300 (1930).

[6] W. W. Watson, Phys. Rev. **32**, 600 (1928).

TABLE II. *Quantum assignments in the* $^1\Sigma \rightarrow {}^1\Sigma$ *system of* BeH^+.

	(2,5)		(3,6)		(3,7)	
J''	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$
1		32,052.46		31,710.60		
2	31,987.36	057.21		713.36	30,010.50	30,077.1
3		057.21		713.36	29,988.32	081.6
4		053.56	31,590.60	710.60	961.96	081.9
5	895.47	045.53	556.23	702.18	932.19	078.7
6	855.88	032.34	518.94	692.26	899.69	072.00
7	812.53		478.64	677.24	864.13	063.16
8	764.87	31,994.51	434.43	658.17	825.54	050.79
9	713.36		386.71	636.70	784.70	034.25
10	658.17		335.42	610.72	740.51	014.76
11	599.10		280.93	581.15	693.17	29,993.94
12	536.08	868.35	224.00	547.84	644.58	969.32
13	470.06	826.97	163.26	511.12	593.00	941.78
14	399.93	781.31		470.06	538.85	911.60
15	326.60	732.25	031.06	427.24	483.00	878.80
16	250.42	679.67	30,960.92	380.45	424.63	843.53
17	170.59	623.01	888.32	330.94	364.18	806.54
18	088.32	563.51		277.64	302.64	766.09
19	003.38	500.70		222.00	238.98	724.01
20	30,915.75	434.43		163.26	173.90	680.08
21	825.46	365.45		102.30	107.88	634.43
22	733.37	293.80		039.32	040.61	589.00
23	639.28	219.35		30,973.63	28,972.78	538.85
24	542.44	142.49		904.86	904.23	488.97
25	444.35	063.37			835.19	
26	344.92	30,982.21			765.81	
27	244.01	899.29			696.89	
28		815.05			628.11	
29					560.09	
30					492.52	

	(4,8)		(5,9)		(6,10)	
J''	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$
1						
2						
3						
4					29,512.65	29,622.19
5	29,733.33	29,876.24			490.59	625.67
6	703.80	872.02	29,561.69	29,725.44	466.94	625.67
7	671.53	865.27	530.63	721.71	441.74	625.67
8	636.64	855.92	500.04	714.29	413.52	620.80
9	599.56	843.53	466.66	703.80	385.16	615.33
10	559.70	828.45	431.55	693.17	354.97	608.09
11	518.40	810.63	394.90	680.08	323.32	599.93
12	474.55	790.90	356.48	664.51	290.36	588.86
13	428.62	768.60	316.49	647.38	256.74	577.58
14	380.70	744.10	274.96	628.31	222.11	564.65
15	331.09	717.97	232.32	608.09	186.02	549.90
16	280.02	688.62	187.87	585.00	149.50	534.66
17	227.37	657.64	143.67	561.69	112.83	518.40
18	173.90	625.67	097.73	536.80	075.45	500.04
19	118.50	591.07	051.77	510.54	038.36	483.00
20	062.51	555.23	005.01	483.00	001.17	464.05
21	005.81	518.40	28,957.97	455.54	28,964.48	445.55
22	28,948.63	480.69	911.12	426.87	928.15	426.87
23	891.18	441.74	864.31	398.16	892.70	408.41
24	833.60	402.24	818.09	369.13	858.46	389.77
25	776.07	362.12	772.61	340.04	825.60	373.34
26	718.97	321.69	728.07	311.64	794.46	
27	662.45	280.02	684.87			
28	606.84	238.98	642.83			
29	552.62					
30	499.52					

TABLE III. *Band origins in the* $^1\Sigma \rightarrow {}^1\Sigma$ *BeH+ system.*

(v', v'')	ν	(v', v'')	ν
0,0	39,051.4	2,5	32,028.26
0,1	36,911.5	3,0	43,284.5
0,2	34,852.5	3,6	31,682.46
0,3	32,875.3	3,7	30,048.86
1,0	40,496.4	4,0	44,621.7
1,3	34,320.4	4,8	29,841.10
1,4	32,426.9	5,9	29,689.23
2,0	41,908.3	6,10	29,587.06

TABLE IV. *BeH+ constants from the rotational term differences.*

v'	B_v'	$-D_v'$	v''	B_v''	$-D_v''$
0	7.129		0	10.659	
1	6.988		1	10.346	
2	6.835	0.00060	2	10.028	
3	6.680	0.00060	3	9.701	
4	6.521	0.00060	4	9.373	
5	6.353	0.00062	5	9.019	0.00093
6	6.158	0.00062	6	8.684	0.00099
			7	8.333	0.00098
			8	7.955	0.00097
			9	7.586	0.00103
			10	7.185	0.00106

TABLE V. *BeH+ band constants.*

ELECTRONIC STATE	B_e	α_e	$-\gamma_e$	$-D_e$	ω_e	$\omega_e x_e$	$-y_e\omega_e$	ν_e
$^1\Sigma^+$ (lower)	10.7996	0.2935	0.0049	0.000987	2221.7	39.79	0.021	
$^1\Sigma^+$ (upper)	7.1835	0.1249	0.0054	0.000608	1476.1	14.8	0.038	39,417.0

should come at $53,113.8 - 1987.5 = 51,126.3$ cm^{-1}, and we do observe a series of weaker lines converging to just about this frequency. Because of the incompleteness of the present data on the (1,0) and (1,1) bands, however, we omit their tabulation. The (0,1) band of this system cannot be detected because of the presence of a multitude of lines of the BeH+ spectrum.

It is well known that an increase in the H_2 pressure in the light source tends to introduce the radiation transitions that are eliminated by predissociation at low gas pressure. To study this effect we ran the Be arc with H_2 pressures up to 70 cm, but the very strong pressure broadening of the several higher members of the diffuse series of Be I which lie in this spectral region obliterated the molecular spectrum. Incidentally, several of the Be I and Be II lines on these spectrograms show extremely large pressure broadenings, some shading to the blue, others to the red. The details of these effects should be investigated.

THE BeH+ SPECTRUM

The $^1\Sigma \rightarrow {}^1\Sigma$ system of the BeH+ molecule is very extensive, as already noted, but to date only the more obvious bands in the center portion of the system have been analyzed.[2, 6] In our present search for new BeH spectra in the region from 3100A to 3600A we have added the (2,5), (3,6), (3,7), (4,8), (5,9) and (6,10) bands. The quantum assignments for these bands are given in Table II and the array of known band origins is displayed in Table III. A considerable number of bands of this system remain unanalyzed, but the data now available are complete enough to enable us to calculate all the constants for both electronic states with considerable accuracy.

In Table IV are listed the constants of the rotational energy term formulas for the known vibrational levels. These constants have been determined from the combination differences by the usual semigraphical method. The values of B_v for $v'=0$ and 1 and $v''=0$ to 4 are taken from the work of E. Bengtsson Knave.[2] The constants in the relation $B_v = B_e - \alpha(v+\frac{1}{2}) + \gamma(v+\frac{1}{2})^2$ representing the variation of these B values with v differ somewhat from those given in reference 2, showing the influence of the added data. We can detect no definite variation of D_v with v, and there is no appreciable effect of a fifth power term in the rotational energy in the range of J values available. Cubic terms in the vibrational energy formula are necessary in both states, the coefficients being markedly smaller than those given by Bengtsson. All band constants are collected in Table V. The more rapid decrease of these constants with v for the lower state tends to close up the gap between corresponding constants for the two states, thus accounting for the convergence of the bands in the sequences, the overlapping of structure from different bands and the general complexity of the red end of this spectrum.