Barium Hydride Band Spectra in the Near Infrared

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A BaH band system with principal heads at 8924A and 9017A degraded to the red is $^2\Sigma \rightarrow {}^2\Sigma$ with the same lower $^2\Sigma$ as for the $^2\Pi \rightarrow {}^2\Sigma$ BaH bands in the visible red region. For the upper $^2\Sigma$ state $B_0 = 3.232$, $D_0 = -1.323 \times 10^{-4}$ and $\gamma_0 = -4.84$. This very large spin doubling indicates interaction with a near-lying lower $^2\Pi$ state which computation shows to be the probable upper state of another BaH band observed on the long wave-length side of 10,052A. The nature of the electron configurations in the several BaH states is discussed.

RECENT analyses of the $^2\Pi \rightarrow {}^2\Sigma$ band system of BaH in the interval from 6925A to 6380A discloses[1, 2] a perturbation in the $^2\Pi_{1\frac{1}{2}d}$ levels, thus indicating the existence of another lower-lying excited state and the possibility of other BaH band systems further into the red. Investigation of the photographic infrared region has yielded two new BaH band systems with principal heads at 8924A and 10,052A, both degraded towards longer wave-lengths.

The experimental arrangement for the production of these spectra was similar to that used in the earlier work.[1] The entire near infrared to about 10,400A was photographed first with a prism spectrograph, while using the new Eastman Type B infrared sensitive plates. This preliminary exposure having displayed several band heads in this region, a lengthy exposure was attempted with a Type B plate in the first order of the 21-foot concave grating in a stigmatic mounting. Only a faint head at 9017A with a few accompanying weak band lines to about 9150A, together with another faint band degraded to the red at 10,052A are visible on this spectrogram. An exposure of only about one-half this amount with an Eastman infrared sensitive plate *A* in the region of 9000A, however, produced a well-developed band system with strong heads at 8924A and 9017A with lines registered out to 9225A which is about the long wave-length limit of sensitivity of these plates. Wave-length measurements were made by comparison with second order Fe lines.

Analysis shows this band system around 9000A to be the 0,0 and 1,1 bands of a $^2\Sigma \rightarrow {}^2\Sigma$ transition whose lower state is the same as the $^2\Sigma$ state of the previously examined $^2\Pi \rightarrow {}^2\Sigma$ band. The quantum assignments of the frequencies of the 0,0 band are given in Table I, while Table II contains the combination differences from which the band constants may be computed. The development of the *R*-branches to higher rotational

TABLE I. *Assignment of frequencies for the 8924A* $^2\Sigma \rightarrow {}^2\Sigma$ *(0,0) band of BaH (d indicates a double line;* cm^{-1} *units).*

$J''+\frac{1}{2}$	P_1	R_1	P_2	R_2
1		11,056.97*d*		
2		060.44		
3	11,036.32	063.94	11,039.33	11,089.34
4	026.70	067.12	034.37	097.10*d*
5	016.92	070.24	029.23	104.95*d*
6	006.70	073.07	023.77	112.40
7	10,996.54	075.65	018.25	119.60
8	986.24	077.94	012.42	126.54
9	975.34	080.02	006.44	133.20
10	964.54	081.78	000.16	139.60
11	953.35	083.44	10,993.64*d*	145.71
12	942.18	084.68	987.08	151.54
13	930.59	085.74*d*	980.18	157.12
14	918.82	086.51*d*	973.03	162.34
15	906.99	087.04*d*	965.68	167.31
16	894.88	087.33*d*	958.15	171.99
17	882.65	087.33*d*	950.43	176.33
18	870.25	087.04*d*	942.42	180.40
19		086.51*d*	934.25	184.15
20		085.74*d*	925.78	187.50
21		084.59	917.30	190.61
22		083.23	908.34	193.35
23		081.50	899.24	195.76
24		079.44	890.05	197.85
25		077.08	880.54	199.57
26		074.60	870.99	200.94
27		071.75	861.05	202.00
28		068.51	850.80	202.63*d*
29		064.97		202.82*d*
30		061.22		202.82*d*
31		056.97*d*		202.63*d*
32		052.56		202.33
33		047.72		201.46
34		042.81		200.26
35				198.58
36	11,049.45 = $^RQ_{21}(1/2)$			196.62
37				194.40
38				191.44

[1] W. R. Fredrickson and W. W. Watson, Phys. Rev. **39**, 753 (1932).

[2] A. Schaafsma, Zeits. f. Physik **74**, 254 (1932).

TABLE II. *Combination differences for the 8924A $^2\Sigma\rightarrow{}^2\Sigma$ BaH band. The $\Delta_2F(K)$ values are the average of the second and third columns in each set, and are the ΔF values from which the constants are calculated.*

Lower state combinations					Upper state combinations				
$J''+\frac{1}{2}$	$R_1(J-1)$ $-P_1(J+1)$	$R_2(J-1)$ $-P_2(J+1)$	K''	$\Delta_2F''(K)$	$J''+\frac{1}{2}$	$R_1(J)-P_1(J)$	$R_2(J)-P_2(J)$	K'	$\Delta_2F'(K)$
2	20.65		1	20.65	2			1	
3	33.74		2	33.74	3	27.62	50.01	2	
4	47.02	60.11	3	47.02	4	40.42	62.73	3	45.22
5	60.42	73.33	4	60.27	5	53.32	75.72	4	58.02
6	73.70	86.70	5	73.52	6	66.37	88.63	5	71.05
7	86.83	99.98	6	86.76	7	79.11	101.35	6	83.87
8	100.31	113.16	7	100.14	8	91.70	114.12	7	96.52
9	113.40	126.38	8	113.28	9	104.68	126.76	8	109.40
10	126.67	139.56	9	126.52	10	117.24	139.44	9	122.00
11	139.60	152.52	10	139.58	11	130.09	152.07	10	134.76
12	152.85	165.53	11	152.68	12	142.50	164.46	11	147.28
13	165.86	178.51	12	165.70	13	155.15	176.94	12	159.80
14	178.75	191.44	13	178.63	14	167.69	189.31	13	172.32
15	191.63	204.19	14	191.53	15	180.05	201.63	14	184.68
16	204.39	216.88	15	204.29	16	192.45	213.84	15	197.04
17	217.08	229.57	16	216.98	17	204.68	225.90	16	209.26
18		242.08			18	216.79	237.98	17	221.35
19		254.62			19		249.90		
20		266.85			20		261.72		
21		279.16			21		273.31		
22		291.37			22		285.01		
23		303.30			23		296.52		
24		315.22			24		307.80		
25		326.86			25		319.03		
26		338.52			26		329.95		
27		350.14			27		340.95		
					28		351.83		

quantum numbers than the P-branches is due solely to the falling-off in sensitivity of the plate emulsion in the region of 9225A. Most striking is the record-breaking size of the doubling in the upper $^2\Sigma$ state as evidenced by the large interval of more than 115 cm^{-1} between the R_1-branch and R_2-branch heads. The satellite $^RQ_{21}(1/2)$ line is definitely present separated from the main $R_1(1/2)$ line by some 7.5 cm^{-1}, the doublet interval at $K'=1$. Other satellite branch lines cannot be detected either because of fusion with P-branch lines, since the doubling in the lower state is relatively small, or because of low intensity. The R-branch heads of the 1,1 band occur at 11,111.47 cm^{-1} and 11,003.41 cm^{-1}.

Comparison of the lower state combinations of Table II with those for the $^2\Pi\rightarrow{}^2\Sigma$ BaH band given in reference 1, p. 758 shows that these two band systems have a common lower state. The method of calculation of the constants B_0 and D_0 of the rotational energy expression for each of the states, as well as the constants γ giving the magnitude of the spin doubling, is identical with that used for the similar $^2\Sigma\rightarrow{}^2\Sigma$ band of SrH at 7020A.[3] The values of these constants are given in Table III.

TABLE III. *Constants from the quantum analysis of the 8924A BaH band. (cm^{-1} units.)*

Lower $^2\Sigma$ state	Upper $^2\Sigma$ state
$B_0=3.404(r_0=2.22\text{A})$	$B_0=3.232$
$D_0=-9.61\times10^{-5}$	$D_0=-1.323\times10^{-4}$
$\gamma_0=+0.186$	$\gamma_0=-4.84$

DISCUSSION

The large size of the doubling constant γ in the spin doubling relation $\Delta\nu_{12}(K)=\gamma(K+1/2)$ applied to the upper $^2\Sigma$ state indicates strong interaction with a near-lying $^2\Pi$ state. Since the γ is negative, that state must lie below this $^2\Sigma$ state. Assuming that a relation of pure precession with $l=1$ holds between these two states of BaH, and that the coupling constant A for the $^2\Pi$ state is 640 (the same fraction of the A for the lowest ^3P level of the alkaline earth atom as prevails for

[3] W. W. Watson and W. R. Fredrickson, Phys. Rev. **39**, 765 (1932).

the corresponding CaH and SrH states), calculation[4] indicates the interval $\nu(\Pi, \Sigma)$ between the two states to be about 1700 cm^{-1}. This would place the center of a $^2\Pi \rightarrow {}^2\Sigma$ band with the same lower $^2\Sigma$ state at 9350 cm^{-1} and the $^2\Pi_{1\frac{1}{2}}$ origin of the same at 9670 cm^{-1}. Addition of another, say, 50 cm^{-1} should give the position of the R_2 head as 9720 cm^{-1} or 10,280A. The band head at 10,052A degrading to longer wave-lengths is undoubtedly this computed head, the discrepancy between calculated and observed positions being in fact better than holds for the analogous SrH levels where the constants of the $^2\Pi$ state are accurately known.

This upper $^2\Sigma$ state and the indicated $^2\Pi$ state lying about 9350 cm^{-1} above the lower $^2\Sigma$ are therefore to be interpreted as $\cdots 6p\sigma$ and $\cdots 6p\pi$ respectively, derived from Ba ^3P+H ^2S. The previously reported $^2\Pi$ state at 14,800 cm^{-1} as well as the normal $^2\Sigma$ state must then originate in Ba ^3D+H ^2S. Both the size of the coupling constant A for this $^2\Pi$ level (462 as compared to 832 for the ^3P level of the Ba atom) and its position above $\cdots 6p\pi\,^2\Pi$ constitute evidence in favor of this assignment. The fact that the $\cdots 5d\pi\,^2\Pi$ lies higher accounts for the relative smallness of the p and q constants[1] involved in its Λ doubling and of the γ for the $\cdots 5d\sigma\,^2\Sigma$ normal state. These constants for these two BaH states probably also reflect some interaction with the only other possible low-lying state $\cdots 5d\delta\,^2\Delta$ which may be involved in some rather complicated BaH bands in the green and yellow portions of the visible spectrum.

[4] Reference 1, Eq. (8).