DECEMBER 15, 1935 PHYSICAL REVIEW VOLUME 48

Barium Hydride Spectra in the Infrared

PHILIP G. KOONTZ AND WILLIAM W. WATSON, *Yale University*

(Received September 23, 1935)

Quantum analyses of the (1,0), (1,1) and (2,1) bands of the infrared $^2\Sigma\rightarrow{}^2\Sigma$ system of BaH and some details of the $^2\Pi\rightarrow{}^2\Sigma$ band at 10,300A are presented. The spin doubling constant γ of the upper $^2\Sigma$ state is very large (-4.88) and decreases with increasing molecular rotation, $A \leqq 625$ cm^{-1} for the $^2\Pi$ state, and a perturbation occurs in the $^2\Pi_{\frac{1}{2}d}$ levels at $J=11\frac{1}{2}$.

OF the several band systems of the BaH molecule in the red and photographic infrared regions only the $^2\Pi\rightarrow{}^2\Sigma$ system whose $\Delta v=0$ sequence lies between 6925A and 6380A has been thoroughly analyzed.[1–3] For the infrared systems discovered by one of the writers[4] the analysis of the (0,0) band of the $^2\Sigma\rightarrow{}^2\Sigma$ system with principal head at 8924A together with a necessarily incomplete analysis[5] of the (0,0) $^2\Pi_{1\frac{1}{2}}\rightarrow{}^2\Sigma$ sub-band at 10,000A have been reported. The present paper gives further details of these infrared bands.

The experimental arrangement for obtaining the spectrograms was similar to that used previously. Three hours' exposure, using Eastman I–P plates, was sufficient for good registration of the $\Delta v=0$ and $+1$ sequences of the $^2\Sigma\rightarrow{}^2\Sigma$ system, the dispersion being about 4.9A/mm. With the new I–Z plates and an exposure time of six hours, the (0,0) $^2\Pi_{\frac{1}{2}}\rightarrow{}^2\Sigma$ sub-band between 10,603A and 10,853A could be photographed, but with low intensity. Although a complete quantum analysis of this band is therefore impossible, the measurements do yield some further information about this $^2\Pi$ state.

Table I contains the assignment of frequencies

[1] W. R. Fredrickson and W. W. Watson, Phys. Rev. **39**, 753 (1932).
[2] A. Schaafsma, Zeits. f. Physik **74**, 254 (1932).
[3] G. Funke, Zeits. f. Physik **84**, 610 (1933).
[4] W. W. Watson, Phys. Rev. **43**, 9 (1933).

TABLE I. *Assignment of frequencies for the infrared* $^2\Sigma\rightarrow{}^2\Sigma$ *bands of BaH (cm^{-1} units).*

$J''+\frac{1}{2}$	P_1	P_2	R_1	R_2
		(1,0) BAND		
1				12130.26
2				38.03
3			12121.39	45.62
4	12084.45	12091.38	24.13	52.86
5	74.36	85.63	26.56	59.68
6	63.42	79.58	28.69	66.13
7	52.47	72.89	30.26	72.14
8	41.41	66.47	31.54	
9	29.89	58.91	32.41	82.92
10	17.96	51.39	32.79	87.68
11	05.62	43.44	32.79	92.07
12	11992.91	35.07	32.41	96.03
13	79.88	26.46	31.54	99.54
14	66.45	17.47	30.47	202.54
15	52.46		29.02	05.19
16	38.75	11998.42	27.13	07.41
17	24.48	88.32	24.75	09.21
18	09.83	77.88	21.93	10.35
19	894.90	66.95	18.75	11.41
20	79.49	56.05	15.13	11.71
21	63.83	44.39	11.10	11.71
22	47.87	32.66	06.59	11.41
23	31.78	20.44	01.71	10.35
24	14.94	07.78	096.45	08.70
25	798.08	894.90	90.62	06.67
26	80.83	81.78	84.45	04.19
27	63.25	68.03	77.76	01.27
28	45.54	54.19	70.63	197.78
29	27.28	39.79	63.42	93.79
30	08.76	24.86	55.19	89.35
31	689.99	09.83	46.56	84.43
32		794.44	37.64	78.66
33	51.35	78.71	28.23	
34	31.75	62.38	17.96	
35	11.67	45.54	08.23	
36	591.32	28.45	11997.23	
37	70.69	10.82	85.76	
38	49.68	693.02	73.79	
39	28.27	74.23	61.30	
40	06.48		48.80	
41	484.57			
42	62.55			

$J''+\frac{1}{2}$	P_1	P_2	R_1	R_2
		(1,1) BAND		
1			10975.37	
2		10963.05	78.97	
3	10954.41	58.26	82.40	11006.93
4	46.08	53.41	85.54	14.85
5	36.25	48.25	88.56	22.30
6	26.48	42.87	91.23	29.38
7	16.27	37.35	93.46	36.43
8	06.04	31.49	95.79	43.09
9	895.44	25.57	97.73	49.49
10	84.52	19.30	99.42	55.58
11	73.52	12.78	11000.82	61.28
12	62.36	06.02	01.98	66.94
13	50.88	899.18	02.68	72.14
14	39.44	91.91	03.28	77.06
15	27.30	84.51	03.54	81.51
16	15.33	76.94	03.54	85.85
17	03.10	69.09	03.28	89.96
18	790.69	61.00	02.68	93.62
19	78.04	52.73	01.98	97.00
20	65.24	44.19	00.82	100.02
21	52.14	35.43	10999.42	02.70
22	38.82	26.53	97.73	05.02
23	25.79	17.36	95.79	07.00
24		07.98	93.46	08.59
25		798.30	90.80	09.90
26		88.40	87.79	10.48
27		78.02	84.58	11.49
28		67.99	80.98	
29		57.41	77.10	
30			73.09	
31			68.29	
32			63.41	

$J''+\frac{1}{2}$	P_1	P_2	R_1	R_2
		(2,1) BAND		
1				12017.47
2				25.40
3			12009.14	32.69
4			11.69	39.59
5	11962.91		14.11	46.32
6	52.46		15.95	52.47
7	41.72	11961.30	17.47	58.16
8	30.55	54.39		63.42
9	19.07	47.30		68.36
10	07.27	39.58	19.39	72.89
11	894.90	31.60	19.39	76.87
12	82.21	23.30		80.46
13	69.41	14.71	17.96	83.71
14	56.17	05.54	16.67	86.41
15	42.63	896.16	14.11	88.78
16	28.87	86.29	12.39	90.62
17	13.69	76.19	09.79	92.03
18	799.41	65.66	06.77	93.01
19	84.50	54.79	03.31	93.39
20	69.21	43.51	11999.42	93.39
21	53.55	31.78	95.10	93.01
22	37.54	19.90	90.32	92.03
23	21.25	07.59	85.05	90.62
24	04.65	794.87	79.52	88.78
25	687.67	81.68	73.31	86.41
26	70.39	68.36	66.45	83.41
27	52.67	54.50	59.75	79.74
28	34.73	40.30	52.46	75.84
29	16.49	25.68	44.39	71.46
30	597.85	10.82	35.73	66.47
31	79.03	695.40	26.87	60.83
32	59.61		17.49	55.19
33	40.22	63.44	07.78	48.62
34	20.12	47.38	897.76	41.41
35	499.89	30.77		33.97
36	79.20	13.37		
37	58.29			
38	36.83			

for the branches of the (1,0), (1,1) and (2,1) bands of the $^2\Sigma \rightarrow {}^2\Sigma$ system. These assignments have been made with the aid of the usual combination differences between the several bands of this and the $^2\Pi \rightarrow {}^2\Sigma$ system in the visible red, the lower $^2\Sigma$ state being common to both. The constants of the rotational energy terms are evaluated from the averages of the $\Delta_2 T_1$ and $\Delta_2 T_2$ differences by the semigraphical method in every case. We list these constants for the two $^2\Sigma$ states in Table II. Our values $B_0 = 3.3496$ and

TABLE II. *Constants from the quantum analysis of the infrared $^2\Sigma \rightarrow {}^2\Sigma$ system of BaH (cm^{-1} units).*

Normal $^2\Sigma$ state	Upper $^2\Sigma$ state	
$B_0 = 3.3496$	$B_0 = 3.232$	$\gamma_0 = -4.88$ for $K < 12$
$B_1 = 3.2839$	$B_1 = 3.1609$	$\gamma_1 = -4.78$ "
$D = -1.10 \times 10^{-4}$	$B_2 = 3.0915$	$\gamma_2 = -4.66$ "
$\alpha = 0.066$	$D = -1.11 \times 10^{-4}$	
$\gamma = +0.186$	$\alpha = 0.070$	

$B_1 = 3.2839$ for the normal state agree exactly with the values $B_0 = 3.3495$ and $B_1 = 3.284$ given by Funke.[3]

The most interesting feature of these bands is the large size of the spin doubling in the upper $^2\Sigma$ state. This, the largest doubling recorded for any $^2\Sigma$ state, is due to the strong "pure precession" interaction with the $^2\Pi$ state but 1460 cm^{-1} below it. The magnitude of the Λ-doubling in the $\Pi_{1\frac{1}{2}}$ component of this $^2\Pi$ state is also evidence for this interaction.[5] With increasing rotational energy the constant γ of the spin doubling relation $\Delta\nu_{12}(K) = \gamma(K + \frac{1}{2})$ decreases for all vibrational states, the values for the highest K levels being -4.61, -4.52 and -4.39 for $v = 0$, 1 and 2, respectively. Similar change of the rate of variation of $\Delta\nu_{12}$ with K has been noted in the corresponding $^2\Sigma$ states of CaH and SrH. Probably the perturbing influence of neighboring energy levels is responsible for this departure from the usual linear relation.

Our partial analysis of the $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$ sub-band at 10,600A reveals the following facts. The R_1 and Q_1 branch heads occur at 10,603.33A and 10,746.37A, respectively. In the R_1 branch a perturbation centering at $R_1(10\frac{1}{2})$ is evident. In the discussion of another perturbation in the $^2\Pi_{1\frac{1}{2}c}$ levels at $J = 20\frac{1}{2}$ the nature of the possible perturbing levels has been considered.[5] Upper state combination differences between the R_1 lines and the few P_1 lines observed for low K levels yield the value 3.12 for $B_0{}^*{}_{,-\frac{1}{2}}$. The position of the Q_1 branch head would locate the $^2\Pi_{\frac{1}{2}}$ origin at about 9285 cm^{-1}. Since the $^2\Pi_{1\frac{1}{2}}$ origin comes at about 9910 cm^{-1}, the coupling constant A for this state must be then about 625 cm^{-1}. This agrees fairly well with the value $A = 640$ assumed in our previous discussion of this $^2\Pi$ state.

[5] W. W. Watson, Phys. Rev. **47**, 213 (1935).

DECEMBER 15, 1935 PHYSICAL REVIEW VOLUME 48

Analysis of the Spectrum of Se II

D. C. MARTIN, *Department of Physics, Cornell University*

(Received August 19, 1935)

An analysis of the spectrum of Se II is given with additions and corrections to that by Krishnamurty and Rao. The spectrum of selenium in this investigation was excited in a hollow cathode discharge with a helium atmosphere. Wave-length measurements were made in the region 500 to 2600A with a 1.5-meter grating vacuum spectrograph. New terms belonging to the $4s^24p^25p$ configuration have been found and identified. Several other terms, probably associated with the $4s^24p^24d$ and $4s^24p^25d$ configurations, have been found and J values assigned, but it has been found impossible at present to assign L and S values to them. Tables of all term values and line classifications known at present are listed.

Introduction

THE first extensive investigation of Se II was made by Bloch and Bloch[1] who published quite an accurate and complete list of wave-lengths in the visible and ultraviolet regions of the spectrum from 6679–2197A. Lacroute[2] extended their earlier measurements into the vacuum region to 1235A. Recently two articles

[1] Leon and Eugene Bloch, Comptes rendus **185**, 761 (1927); Ann. de physique **13**, 233 (1930).

[2] M. P. Lacroute, J. de phys. et rad. **9**, 180 (1928).