

## QUANTUM ANALYSIS OF THE BERYLLIUM OXIDE BANDS

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## ABSTRACT

New measurements of the structure lines in the (0, 0), (1, 1), (0, 1), (1, 2), (1, 0) and (2, 1) bands of the visible BeO system are reported. Each band has *P* and *R* branches of almost equal intensity, the lines of which are strictly single. There is probably but one missing line at the origin. This structure characterizes the system as  $^1S \rightarrow ^1S$ , the odd multiplicity agreeing with the even number of electrons in neutral BeO. The rotational terms are investigated by the combination principle, and can be represented by  $F(j) = Bj(j+1) + D[j(j+1)]^2 + \dots$  with *j* integral as required for  $^1S$  states. One perturbation is found, consisting of a displacement of the line *R*(49) in the (1, 0) band by  $0.45 \text{ cm}^{-1}$  toward lower frequencies, with no sign of doubling. The following equation is obtained for the null-lines:  $\nu_0 = 21,254.05 + 1370.81(n' + \frac{1}{2}) - 7.76(n' + \frac{1}{2})^2 - 1487.45(n'' + \frac{1}{2}) + 11.87(n'' + \frac{1}{2})^2$ .

**Molecular constants of BeO.**—The principal molecular constants, evaluated from rotational term-differences using the new quantum mechanics energy formula, are:  $B_0' = 1.5771$ ,  $B_0'' = 1.6514$ ,  $\alpha' = -0.0160$ ,  $\alpha'' = -0.0186$ ,  $D_0' = -8.44 \times 10^{-6}$ ,  $D_0'' = -8.26 \times 10^{-6}$ ,  $\beta' = +0.03 \times 10^{-6}$ ,  $\beta'' = -0.06 \times 10^{-6}$ ,  $F_0' = 22 \times 10^{-12}$ ,  $F_0'' = 12 \times 10^{-12}$ , the zero subscripts referring to the vibrationless condition. The nuclear separation in the final state is:  $r_0'' = 1.327 \times 10^{-8} \text{ cm}$ .

THE spectrum obtained by introducing beryllium or beryllium salts into the arc in air shows a system of bands in the visible region consisting of several sequences which degrade toward the red. The stronger band heads were first measured by Hartley, and later by Lecoq de Boisbaudran and by de Gramont.<sup>1</sup> The spectrum was investigated in more detail by L. C. Glaser,<sup>2,3</sup> using the second order of a 10-foot grating. In addition to more accurate and complete measurements of the heads, Glaser gave a table of the structure lines of the strongest sequence, that in the blue with its first head at  $\lambda 4708$ . The lines of the first band he arranged in four series  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ . As will be shown below, this division cannot be justified, a fact which is not surprising since the work was done before the development of the present theory of band spectra. His attempts to find numerical relations between these bands and the AlO bands of the aluminum arc<sup>4</sup> were doubtless due to the marked similarity of the two spectra in many respects.

According to the view we wish to support, these beryllium bands are also due to the oxide, BeO. Some of Glaser's experiments give evidence for this; in particular he found that with the arc between metallic Be electrodes, the bands are much weaker in vacuum than in air. Further experimental evi-

<sup>1</sup> For a summary and comparison of the earlier results see Kayser and Konen, "Handbuch der Spectroscopie" VII, 102 (1924).

<sup>2</sup> L. C. Glaser, Dissertation, Berlin (1916).

<sup>3</sup> Glaser, Ann. d. Physik 68, 73 (1922).

<sup>4</sup> W. C. Pomeroy, Phys. Rev. 29, 59 (1927).

dence has recently been obtained by Jevons,<sup>5</sup> who finds this group of bands to be relatively stronger in the outer part of the flame surrounding the arc in air. Combining these observations with the theoretical confirmation to be given below, there seems to be little doubt as to the identity of the emitter. The purpose of the present communication<sup>6</sup> is to give the quantum interpretation of the rotational structure of the bands of this system. It is based on new measurements of the lines of the six strongest bands made from plates on which the dispersion and resolution are roughly double those reached by Glaser.

*The spectrograms.* A horizontal carbon arc with both poles cored with a mixture of equal parts of powdered potassium beryllium fluoride and carbon dust proved to be a very satisfactory source. With an average current of about 5 amp, a pale blue flame tinged with yellow appeared above the poles. An image of this flame was thrown on the slit of the 21 foot concave grating

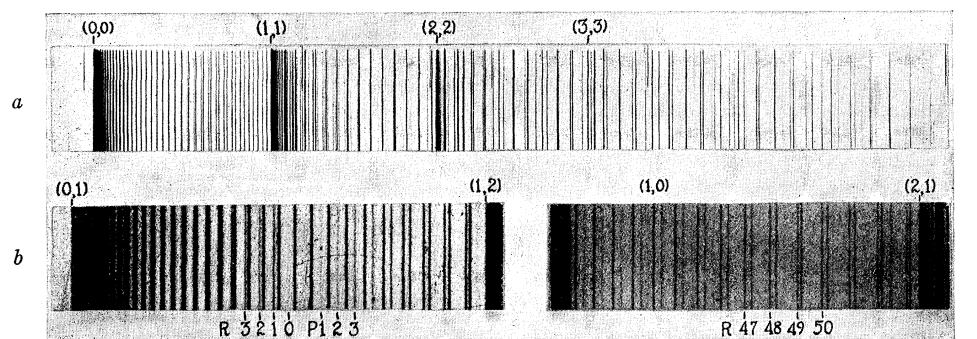


Fig. 1. *a.* Strongest sequence of BeO bands. Iron arc comparison spectrum. *b.* First part of (0, 1) band, showing intensity anomalies near the origin. The line  $R(1)$  is exceptionally strong, while  $R(0)$  is weaker than the corresponding line,  $P(1)$ . *c.* Region  $\lambda\lambda$  4435-4450 of the (1, 0) band. The perturbation of  $R(49)$  shows as a discontinuity in the width of the doublets formed by  $R$  and  $P$  lines.

spectrograph.<sup>7</sup> The spectrum thus obtained consisted of the ultra-violet BeF bands,<sup>8</sup> the BeO bands in the blue and green, and the stronger bands of the green CaF sequence,<sup>9</sup> as well as atomic lines of Be, Ca, Fe, Mn and other impurities. Comparison lines of the iron arc were used<sup>10</sup> and their exact coincidence with the Fe lines appearing in the band exposure eliminated the possibility of accidental shifts.

<sup>5</sup> W. Jevons, Proc. Roy. Soc. (in press). We are indebted to Professor Jevons for making this article available to us in manuscript, as well as a copy of Glaser's work referred to above.<sup>2</sup>

<sup>6</sup> A preliminary account of this investigation was given in a paper before the American Physical Society at the New York meeting, February, 1928, Phys. Rev. **31**, 705 (1928).

<sup>7</sup> The plates were taken by one of the writers (F. A. J.) while a National Research Fellow at Harvard University. The characteristics of the grating and its mounting are described in Phys. Rev. **30**, 438 (1927).

<sup>8</sup> S. Datta, Proc. Roy. Soc. **A101**, 187 (1922).

<sup>9</sup> Datta, Proc. Roy. Soc. **A99**, 436 (1921).

<sup>10</sup> Wave-lengths as given by Meggers, Kiess and Burns, Bull. Bur. Stan. **19**, 263 (1924).

The strong group in the blue (Fig. 1a), according to the vibrational quantum number assignment made by Mecke,<sup>11</sup> is the sequence having  $n'' - n' = 0$ . The two adjacent sequences, +1 and -1, were also suitable for measurement. The +2 sequence found by Glaser and the few bands of the

TABLE I. Lines in the visible BeO bands. The columns of  $\nu_{vac}$  for the lines of each band are headed by its vibrational quantum numbers and  $\lambda_{dir}$  of the band head.

(0,0) band $\lambda 4708.636$			(0,1) band $\lambda 5054.415$		(1,1) band $\lambda 4732.618$		(2,1) band $\lambda 4451.664$		
$j$	$R(j)$	$P(j)$	$R(j)$	$P(j)$	$j$	$R(j)$	$P(j)$	$R(j)$	$P(j)$
0	21,199.81				1				
1	202.88	21,193.25	19,739.14	19,729.70	2	21,097.30			
2	205.74	189.97	742.07	726.39	3	099.76		22,439.22	
3	208.52	186.41	744.89	722.96	4	102.41	21,074.47		
4	211.12	182.66	747.58	719.36	5	104.82	070.69	444.00	22,410.20
5	213.58	178.88	750.21	715.73	6	107.12	066.71	446.14	
6	215.58	174.82	752.63	711.95	7	109.19	062.61	447.93	401.84
7	217.71	170.65	754.96	708.02	8	111.20	058.37	449.68	397.49
8	219.65	166.35	757.19	704.04	9	112.99	054.02	451.23	392.84
9	221.43	161.93	759.40	699.92	10	114.68	049.50		388.11
10	223.12	157.28	761.48	695.70	11	116.32	044.91		383.11
11	224.62	152.57	763.43	691.45	12		040.13	454.75	378.03
12	225.92	147.70	765.30	686.89	13	118.65		455.47	372.76
13	227.23	142.69	767.03	682.33	14	120.05	030.17	456.18	367.29
14	228.40	137.53	768.64	677.82	15			456.70	361.70
15	229.34	132.22	770.12	673.05	16			457.23	355.95
16	230.08	126.75	771.51	668.22	17				350.00
17	230.67	121.01	772.79	663.26	18				343.89
18	230.94	115.39	773.95	658.20					
19		109.40	774.98	653.06	(1,0) band $\lambda 4427.312$		(1,2) band $\lambda 5075.726$		
20	231.61	103.48	775.90	647.79	$j$	$R(j)$	$P(j)$	$R(j)$	$P(j)$
21	231.61	097.30	776.68	642.40	0	22,555.06		19,651.13	
22		090.96	777.37	636.95	1	558.23		654.04	
23	230.94	084.52	777.92	631.35	2	560.82		657.07	19,641.47
24	230.67	077.93	778.40	625.65	3	563.51		659.76	638.05
25	230.08	071.17	778.84	619.92	4	565.93		662.56	634.56
26	229.34	064.31	779.18	614.00	5	568.11	22,534.03	665.09	630.93
27	228.40	057.30	779.18	608.04	6	570.16	529.79		627.28
28	227.53	050.17	779.18	601.94	7	571.98	525.41	669.89	623.43
29	226.33	042.88	779.18	595.66	8	573.67	520.90	672.26	619.48
30	224.94	035.41	778.84	589.35	9	575.17	516.23	674.46	615.40
31	223.48	027.85	778.40	582.92	10	576.49	511.34	676.57	
32	221.75	020.03	777.37	576.38	11	577.65	506.27	678.55	607.29
33	219.95	012.30	777.37	569.76	12	578.57	501.08	680.49	602.81
34	218.01	004.20	776.68	563.04	13	579.29	495.63	682.32	598.54
35	215.97	996.02	775.90	556.20	14	579.87	490.09	683.93	594.06
36	213.58	987.65	774.98	549.24	15	580.30	484.34	685.52	589.36
37	211.12	979.40	773.95	542.27	16		478.39	686.98	584.61
38	208.52	970.73	772.79	535.08	17	580.79	472.16	688.32	579.73
39	205.74	962.02	771.51	527.90	18		466.09	689.60	575.01
40	202.88	953.18	770.12	520.51	19	580.30	459.64	690.70	569.84
41	199.81	944.17	768.64	513.02	20	579.87	452.83	691.71	564.85
42	196.56	935.02	767.03	505.50	21	579.12	446.14	692.64	559.73
43	193.25	925.77	765.30	497.86	22	578.28	439.22		
44	189.67	916.36	763.43	490.05	23	577.25	432.17		
45	185.94	906.74	761.48	482.23	24	576.06	424.86		
46	182.11	897.07	759.40	474.37	25	574.68	417.33		
47	178.16	887.12	757.19	466.16	26	573.10	409.68		
48	173.97	877.08	754.80	458.01	27	571.35	401.84		
49	169.61	867.05	752.33	449.75	28	569.43	393.84		
50	165.15	856.75	749.71	441.39	29	567.30	385.64		
51	160.53	846.37	747.00	432.89	30	564.94	377.32		
52	155.72	835.82	744.19	424.31	31	562.47	368.76		
53	150.73	825.20	741.25	415.66	32	559.76	360.13		
54	145.57	814.25	738.17	406.89	33	556.95	351.19		
55	140.29	803.32	735.00	398.01					
56	134.87	792.21	731.67	389.03					
57	129.25	780.97	728.23	379.92					
58	123.58	769.48	724.65	370.72					
59	117.51	758.09	721.00	361.49					
60		746.40							
61		734.59							

-2 sequence recently added by Jevons<sup>5</sup> are very faint. Accordingly, measurements have been made of the lines of the first two bands in each of the three stronger sequences, using the second order except for the (0, 1) and (1, 2)

<sup>11</sup> R. Mecke, Phys. Zeits. 26, 217 (1925).

bands, which were measured in the first order. The mean error for each line should not in general exceed  $0.03 \text{ cm}^{-1}$ . In some instances, however, because of superposition by atomic lines (particularly in the  $-1$  sequence) and by other strong band lines, larger errors were unavoidable. Table I contains the wave-numbers in vacuum of all lines measured. In view of these numerous cases of superposition and overlapping of series, the intensity data are of very little value and have therefore been omitted.

*Structural features of the bands.* Since the bands of each sequence are closely grouped, the system is of the familiar type in which the vibration frequency and moment of inertia are only slightly changed by the electron transition. The vibrational intensity distribution is also characteristic of this type, resembling that of the violet CN bands in the arc. Hence there could be no doubt as to the correct assignment of vibrational quantum numbers. A complete description of the vibrational structure is given by Jevons<sup>5</sup> who finds that the heads are closely represented by:

$$\nu_n = 21,287.0 + 1364.2(n' + \frac{1}{2}) - 5.90(n' + \frac{1}{2})^2 - 1479.1(n'' + \frac{1}{2}) + 15.22(n'' + \frac{1}{2})^2 - 5.24(n' + \frac{1}{2})(n'' + \frac{1}{2}) \quad (1)$$

The rotational structure is of the simplest possible type, each band having one  $R$  and one  $P$  branch of strictly single lines. Resolution is complete except for 4 or 5 lines at the head, and in the  $(0, 0)$  band about 70 members of each branch can be traced reaching a maximum of intensity between  $j = 30$  and 35 and extending over several other bands of the sequence. There is no sign of splitting into finer components even for the last lines. The  $\alpha$  and  $\beta$  series of Glaser together make up the  $P$  branch, alternate lines belonging to one or the other. His  $\gamma$  and  $\delta$  series form the  $R$  branch in a similar way.

Difficulty was encountered in establishing the number of missing lines, although the bands are well resolved in the neighborhood of the origin, which is far from the head. In the  $(0, 0)$  band, coincidence with the  $R$  lines returning from the head prevents any decision. The region of the origin in the  $(1, 0)$  band is obscured by a diffuse atomic line. The best evidence was obtained from the  $(0, 1)$  band. Here it appears that but one line is missing, although the first  $P$  line is extremely weak, and the first  $R$  line even stronger than two subsequent lines of this branch (Fig. 1*b*). The latter anomaly is very probably due to coincidence with the Ti line  $\lambda 5064.66$ . No evidence was found of a  $Q$  branch, although a systematic search was made for  $Q$  lines of low intensity.

In the  $(1, 0)$  band a perturbation occurs which is obvious even on casual inspection (Fig. 1*c*). The line  $R(49)$  is displaced  $0.45 \text{ cm}^{-1}$  toward lower frequencies from its expected position. The fact that no splitting or intensity change occurs is further evidence for the true singlet character of the lines. The corresponding line in the  $(0, 0)$  band is not perturbed, so the irregularity must be in the initial state  $n' = 1, j' = 50$ .

*Rotational term analysis.* Calling the first lines of the two branches  $R(0)$  and  $P(1)$  it was found at once that the combination relations between the  $R$

and  $P$  branches<sup>12</sup> agreed among the bands in the manner to be expected. The extent of this agreement is shown graphically in Fig. 2. The combination differences  $\Delta_2 F$  for low quantum numbers are represented closely by  $4B(j+\frac{1}{2})$  where  $j=0, 1, 2, \dots$ . Since there is probably only one line missing near the origin and since the bands show no evidence of electronic multiplicity, the assumption is justified<sup>13</sup> that there is no resultant electronic angular momentum in either initial or final states. Hence the system arises from a transition

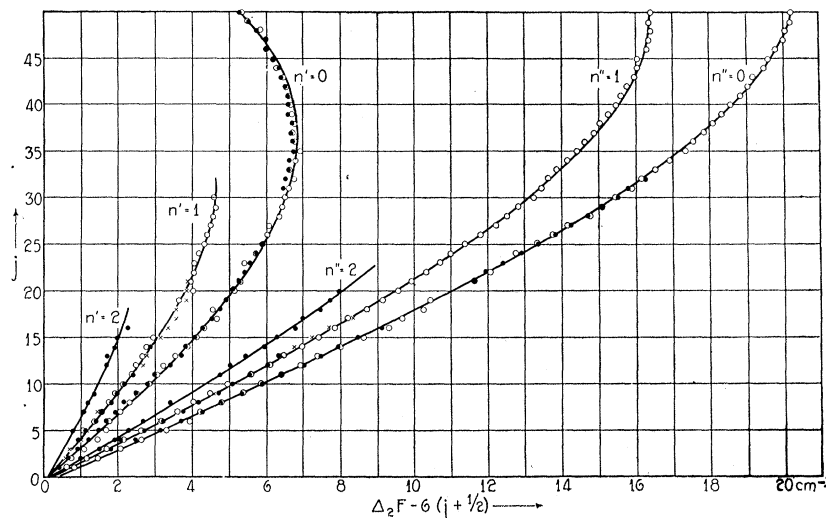


Fig. 2. Combination differences. The solid lines represent the values calculated by Eqs. (2) and (3). The linear function  $6(j+\frac{1}{2})$  has been subtracted from  $\Delta_2 F$  to magnify the scale. For the initial states circles, dots and crosses represent data from bands having  $n''=0, 1$  and  $2$ , respectively. Similarly, for the final states they refer to bands with  $n'=0, 1$  and  $2$ .

between two  $^1S_0$  molecular terms and is strictly analogous to the CuH bands. In a  $^1S$  state the accurate expression for the rotational term-difference is, using the  $j$  values of the new quantum mechanics,

$$\Delta_2 F(j) = 4B_n(j+\frac{1}{2}) + 8D_n(j+\frac{1}{2})^3 + 12F_n(j+\frac{1}{2})^5 + \dots \quad (2)$$

Following the method suggested by Birge<sup>14</sup> the constants  $B_n$  were evaluated by least squares, using the theoretical relations for  $D_n$  and  $F_n$ .<sup>15</sup> The results of this calculation are

$$\begin{aligned} B_n' &= 1.5771 - 0.016(n'+\frac{1}{2}), & B_n'' &= 1.6514 - 0.0186(n''+\frac{1}{2}), \\ D_n' &= \{-8.44 + 0.03(n'+\frac{1}{2})\} 10^{-6} & D_n'' &= \{-8.26 - 0.06(n''+\frac{1}{2})\} 10^{-6} \\ F_n' &= 22 \times 10^{-12} & F_n'' &= 12 \times 10^{-12}. \end{aligned} \quad (3)$$

<sup>12</sup> R. T. Birge, Bull. Nat. Res. Council No. 57, p. 145 (1926).

<sup>13</sup> R. S. Mulliken, Phys. Rev. **28**, 481 (1926).

<sup>14</sup> Ref 12, p. 174.

<sup>15</sup> Account was taken of the variation of  $D_n$  with  $n$  (ref. 4, Eq. (19)).  $F_n$  was taken as the same for  $n=0, 1$  and  $2$ .

From the constant terms in the equations for  $B_n$ , the following values of the moment of inertia  $I_0$  for the vibrationless molecule and of the corresponding internuclear distances  $r_0$  are obtained:

$$I_0' = 17.564 \times 10^{-40} \text{ gr cm}^2 \quad I_0'' = 16.774 \times 10^{-40}$$

$$r_0' = 1.358 \times 10^{-8} \text{ cm} \quad r_0'' = 1.327 \times 10^{-8}$$

$B_n$  was evaluated separately for each band, and the agreements shown in Table II furnish conclusive evidence that the assignment of vibrational numbers is correct. This table also includes the band-origins,  $\nu_0$ , each of which is

TABLE II. *Band constants*

	$n'' = 0$	1	2
$n'$	$B' = 1.5692$	1.5689	
0	$B'' = 1.6421$	1.6232	
	$\nu_0 = 21,196.76$	19,732.99	
1	1.5534	1.5537	1.5537
	1.6422	1.6233	1.6052
	22,552.15	21,088.28	19,648.00
2		1.5363	
		1.6231	
		22,428.20	

the mean of a set of values obtained from several lines of both  $R$  and  $P$  branches. By the term formula used,  $\nu_0$  is the same as the wave-number of the null-line. The origins are quite accurately given by the equation:

$$\nu_0 = 21,254.05 + 1370.81(n' + \frac{1}{2}) - 7.76(n' + \frac{1}{2})^2$$

$$- 1487.45(n'' + \frac{1}{2}) + 11.87(n'' + \frac{1}{2})^2 \quad (4)$$

*Conclusions.* The constants of the vibrational energy from Eq. (4) differ markedly from those given by Jevons (Eq. (1)). This is to be expected, since his equation refers to heads, which in the present case are at a rather large, and therefore variable, distance from the origins.

As was mentioned above, the rotational structure conforms in every respect with that to be expected for a band system resulting from a  $^1S \rightarrow ^1S$  electron transition. The odd multiplicity requires<sup>13</sup> that the emitting molecule have an even number of electrons. This definitely excludes BeN and BeH, leaving as possibilities Be<sub>2</sub> or BeO, since ionized molecules do not come into consideration. The experimental evidence favors BeO, as do considerations of stability. The internuclear distance in the final state, the lowest known level of BeO, as compared with the corresponding  $r_0$  values for the oxides of the other elements in the first row of the periodic table seems entirely consistent with this view:

	BeO	BO	CO	NO	O <sub>2</sub>
$r_0''$	1.33	1.21	1.15	1.15	1.20

All of these refer to the normal electronic state, and they evidently show the same general trend as the atomic volume curve for these elements.

NEW YORK UNIVERSITY,  
UNIVERSITY HEIGHTS, N. Y.,  
November, 1928.

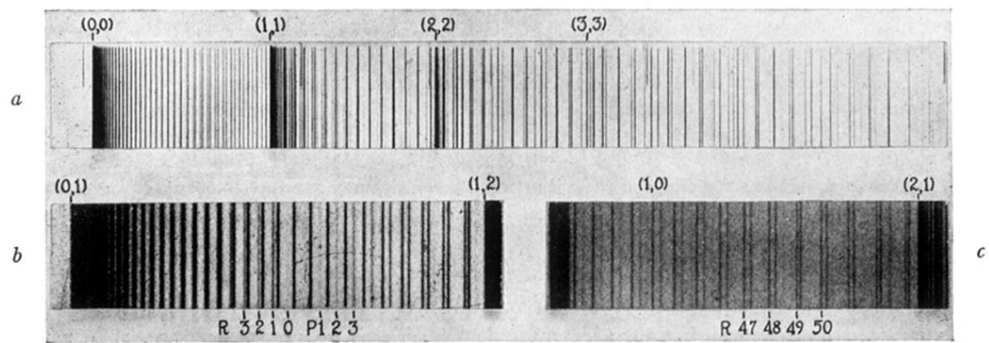


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