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THE ISOTOPE EFFECT IN BAND SPECTRA, II: THE SPECTRUM OF BORON MONOXIDE

By Robert S. Mulliken[1]

Abstract

Band spectrum of boron monoxide.—Previous measurements of Jevons on the BO bands (ascribed by him to BN) have been extended, with the help of *new spectrograms*. Over 100 β and about 200 α heads were measured or identified and are tabulated with their intensities. (1) Complete *verification of the predicted vibrational isotope effect* is found for both α and β systems. Each is composed of two closely similar superposed systems, of which the weaker and larger scale one is due to the less abundant isotope $B^{10}O$, the other to $B^{11}O$. There was no indication of any other B isotopes than B^{10} and B^{11}. The measured positions of all the heads can be represented by the equations:

$$B^{10}O:\ \nu_\alpha = \begin{Bmatrix} 23{,}652.2\ ;\ 23{,}638.9 \\ 23{,}526.0\ ;\ 23{,}512.7 \end{Bmatrix} + 1285.6n' - 11.7n'^2 - 1926.8n'' + 12.21n''^2$$

$$B^{11}O:\ \nu_\alpha = \begin{Bmatrix} 23{,}661.6\ ;\ 23{,}648.3 \\ 23{,}535.4\ ;\ 23{,}522.1 \end{Bmatrix} + 1247.9n' - 10.6n'^2 - 1873.2n'' + 11.68n''^2$$

$$B^{10}O:\ \nu_\beta = 42{,}874.6 - 0.19n'n'' + 1304.6n' - 10.43n'^2 - 1927.9n'' + 12.66n''^2$$

$$B^{11}O:\ \nu_\beta = 42{,}880.9 - 0.17n'n'' + 1268.8n' - 9.98n'^2 - 1872.9n'' + 11.84n''^2$$

For the linear terms in n' and n'' (the initial and final vibrational quantum numbers), the weighted mean ratio for corresponding coefficients of the two isotopes is 1.0291 ± 0.0003; for the quadratic terms, 1.062 ± 0.008. The theoretical values are 1.0292 and 1.059 for BO, 1.0276 and 1.056 for BN. The complete agreement with theory for BO, but not for BN, in the absence of contradiction from more direct experimental evidence, makes practically certain the BO origin of the bands, and at the same time quantitatively confirms the predicted vibrational isotope effect and gives powerful new support to the quantum theory of band spectra. Further evidence supporting the assignment of the bands to BO is presented. A comparative *energy-level diagram* for both isotopes is given, showing also the existing transitions with their intensities. The α and β systems correspond to the same final state of the BO molecule, which is in all probability its normal state. (2) The inequality of the constant terms for the two isotopes in the above equations indicates an electronic isotope effect of wholly unprecedented magnitude. This vanishes, however, if one makes the assumption that the minimum values of n' and n'' are not zero, but $\frac{1}{2}$. This result makes probable the existence of *half-integral vibrational quantum numbers* in BO, and of a *null-point vibrational energy* of $\frac{1}{2}$ quantum for BO (and doubtless for other molecules). (3) Measurements on the structure lines of three β bands gave an approximate confirmation of the *rotational*

[1] National Research Fellow.

isotope effect. (4) They also permitted a partial *analysis of the band structure*, so that approximate equations for the origins of the α and β bands were obtained, as well as values for the internuclear distance for BO. (5) Measurements are given on a *new system of BO bands* of low intensity lying in the visible, and corresponding to a transition from the β initial state to two (probably the first and third) of the four α initial states. The agreement with calculation is very close for both isotopes (on the assumption that the new bands consist of Q branches). This result confirms the preceding analyses of the α and β systems. The grouping of the new bands is of an unusual type, due to the values of the constants involved. (6) *Comparison of the arc and active nitrogen spectra of BO.* The β bands, when generated in active nitrogen, appear to consist usually of an isolated positive branch. A negative branch appears to be weakly present in a few cases. In the arc, doublets appear in place of the single positive branch lines, a new component being added. The intensity distribution of the BO bands in active nitrogen among various n' and Δn values is discussed. The n' distribution, unlike the m' distribution, corresponds to a high effective temperature.

Possible analogy of BO and CN to the Na atom.—If the α and β systems of BO, and the red and violet CN bands, are respectively analogous to the first two members of the principal series of Na, the *electronic resonance potentials* of BO at 2.9 and 5.3 volts (calculated from the constant terms of the above equations), and of CN at 1.8 and 3.2 v, may be compared with the values 2.10 and 3.74 for Na. The weakness of the transition $\beta \rightarrow \alpha$ in BO is then analogous to that of the "forbidden" transition $2p-3p$ in Na. BO and CN, like Na, have nine outer electrons (outside the nucleus and K electrons) of which the first eight possibly form an octet somewhat as in Na, leaving the ninth in a loosely bound orbit. If the preceding analogy is correct, BO and CN should have *ionizing potentials* at about 7.0 and 4.4 volts, respectively (Na ionizes at 5.1 v). If this is true the alternation from higher to lower ionization potentials observed in the case of atoms, according as the number of electrons is even or odd, also holds for the series of molecules BO, CN, N_2^+; CO, N_2; NO; O_2, with 9, 10, 11, and 12 outer electrons, respectively.

QUALITATIVE CONFIRMATION OF THE VIBRATIONAL ISOTOPE EFFECT IN THE BAND SPECTRUM OF BORON MONOXIDE

IN a previous paper[2] the subject of the isotope effect in electronic band spectra has been discussed from a general and theoretical standpoint on the basis of the quantum theory. In the following pages this paper will be referred to as (I). Reference should be made to (I) for the notation and terminology here used. The present paper deals with the confirmation[3] of some of the predictions of the theory, in the case of a band spectrum which was originally ascribed to boron nitride[4] but which the present writer now attributes to a compound boron monoxide.

[2] R. S. Mulliken, Phys. Rev., **25**, 119 (February, 1925).

[3] Preliminary accounts by the writer have appeared in Science, Aug. 31, 1923 (BN accepted as emitter); Nature, March 22, 1924 (BO; SiN is also discussed here); Nature, September 6, 1924 (evidence as to BO vs BN; half vibrational quantum numbers).

[4] W. Jevons, Proc. Roy. Soc. **91A**, 120-134 (1914).

Either BN or BO would have an unusually favorable value of $(\rho-1)$, the isotope coefficient [cf. (I), Eqs. (11), (16)]. It may be recalled that $\rho=\sqrt{(1/M_2+1/M')/(1/M_1+1/M')}$, where M_2 and M_1 are the atomic weights of the less abundant and the more abundant isotope, respectively, and M' is that of the other element. According to Aston,[5] boron contains two isotopes of atomic weights 10.0 and 11.0. According to the chemical atomic weight, 10.82, as recently determined by Baxter and Scott[6] and by Hönigschmidt and Birkenbach,[7] isotope 11 must be 4.6 times as abundant as isotope 10. Accordingly the band spectrum of BO should consist of two superposed spectra, the stronger due to $B^{11}O$, the weaker to $B^{10}O$.

The band spectrum here ascribed to BO was first obtained by Lord Rayleigh in 1913, by the reaction of BCl_3 vapor with active nitrogen. The heads from λ2100 to λ6400 were then measured by Jevons,[4] using photographs taken with Hilger glass and quartz spectrographs of moderately high dispersion. Jevons gives a good set of reproductions of the spectrum. This consists of two band systems. The α system of Jevons is a doubly double-headed system extending probably from about λ12000, certainly from λ8500, to below λ3100.[8] The relative spacing and intensities of the α heads are well shown in a diagram by Jevons. The single-headed β system extends from near λ3700 to below λ2100.[8] In both systems the heads are shaded toward the red, and are sharply defined. Jevons was able to express the positions of the heads of each system in terms of a Deslandres equation. In addition to the main systems of bands, Jevons found some fainter bands, most of which he grouped in two "subsidiary systems," β_1 and β_2, related to the main β system.

Granting that a difference exists between isotopes, the main α and β systems of Jevons should obviously be ascribed to the more abundant isotope $B^{11}O$. According to the theory, every $B^{11}O$ band should be accompanied by a $B^{10}O$ band about one fifth as intense, forming an α′ and a β′ system. The α and α′ systems should have a *common origin*;[2] on either side of this origin each $B^{10}O$ band should be at a distance about 2.9 per cent greater than the corresponding $B^{11}O$ band, since $(\rho-1)=0.0292$. The same statement holds for the β and β′ systems.

[5] F. W. Aston, "Isotopes", London, Edw. Arnold Co., 2nd ed., 1924.

[6] Baxter and Scott, Proc. Am. Acad. Arts Sci. **59**, 21 (1923).

[7] Hönigschmidt and Birkenbach, Anales Soc. Españ. Fís. Quim. **20**, 167 (1922); also, Stock and Küss (Ber. Deutsch. Chem. Ges. **56B**, 314, 1923) get a preliminary value 10.81.

[8] Jevons' identified data cover the range λ 6370-3370 for the α system, and λ 3256-2140 for the β system.

Assignment of vibrational quantum numbers. Before attempting to verify these predictions with Jevons' data, it is necessary to assign vibrational quantum numbers to the α and β bands. This can readily be done with the aid of two criteria of Heurlinger and Kratzer, (I) p. 136. (It could also be done, (I), p. 136, with the aid of the isotope effect, if it were assumed in advance that the latter would be in accordance with theory.) Jevons arranged the bands in a rectangular diagram (m vs p)—compare the rather similar arrangement of the circles containing estimated intensities of bands, in Fig. 1—in such a way that it is necessary only to change his empirical designations $n=62,61 \ldots 57$ for the β system to $n'=0,1, \ldots 5$; and $p=79,78 \ldots 69$ to $n''=0,1, \ldots 10$, where n' and n'' are the vibrational quantum numbers for the initial and final states, respectively. For the α system, the change is from $m=61, 60, \ldots 56$ to $n'=0,1, \ldots 5$, and from $p=79, 78, \ldots 74$, to $n''=0,1, \ldots 5$. A corresponding transformation can be made in Jevons' formulas for the band-heads.

Confirmation of isotope effect with Jevons' data. The α and β system origins for $B^{11}O$ can now be located. Jevons' β_2 bands on the high frequency side and his β_1 bands on the low frequency side of the β origin fulfill the requirements for $B^{10}O$ in respect to both position and intensity. Jevons' reproduction shows this well. His β_1 and β_2 bands evidently become more and more separated from the corresponding (adjacent) β bands with increasing distance from the origin ($m=62$, $p=79$). The results afford an excellent qualitative confirmation of the vibrational isotope effect, as will be seen by comparison with a theoretical diagram [(I) Fig. 1 (a)]. However, not all the expected $B^{10}O$ β bands, and none of the $B^{10}O$ α bands, are to be found in Jevons' data. The only evidence for $B^{10}O$ α heads consisted in some faint indications at the red end of the spectrum in Jevons' reproduction (not in his data), and a few unidentified measured heads in the ultraviolet.[9]

Confirmation with new data. The BO bands have now all been remeasured, extending Jevons' data into the near infra-red, and slightly in the ultraviolet. Many weak heads not recorded by Jevons have been measured, especially those due to $B^{10}O$. Careful examination and

[9] It is not surprising that the heads referred to at the red end were passed by in the absence of a guiding theory, since they are heavily masked by structure lines of the neighboring strong $B^{11}O$ heads (cf. Plate I(d) and Fig. 2). The masking is even more complete throughout the central part of the system; this is due particularly to the quadruplet character of the system. The bands of the two isotopes are well separated in the infra-red and also in the ultra-violet, but Jevons did not reach the former region, and in the latter the CN bands apparently interfered.

measurement of the photographs taken in this connection show in every case, so far as can be determined, with two or three doubtful exceptions, a $B^{10}O$ head, of about the correct intensity, for each $B^{11}O$ head, in both α and β systems. This may be seen by reference to the wave-length tables below (Tables I and II). Confirmation of the vibrational isotope effect for each of a very large number of bands is thus obtained in the present work, as compared with its former confirmation in the case of only a *single* infra-red HCl band.[10]

In the identification on the $B^{10}O$ heads, the procedure was first to calculate their positions, using for each $B^{10}O$ system a formula obtained by theory from the corresponding formula for $B^{11}O$. The calculation was made originally on the assumption that BN was the emitter of the bands. The much better agreement with BO became apparent only after careful measurements [cf. Eqs. (1) and (2)], since $(\rho-1)=1.0276$ for BN, as compared with 1.0292 for BO.

Plate I shows enlargements of various portions of the BO spectrum. Plate I (b) shows the $(2\rightarrow 2)$ β bands near the origin, and (a) shows other β bands farther away. It will be seen that the pattern of the band lines from each $B^{11}O$ head is repeated in lower intensity for the corresponding $B^{10}O$ head. Plate I (e) shows this on a larger scale for the $(0\rightarrow 1)$ band. In (c) the $(3\rightarrow 0)$ and $(2\rightarrow 0)$ α bands show well the isotope effect on the ultraviolet side of the α system. The pattern of the two stronger ($B^{11}O$) head-pairs is repeated, with a shift toward the violet, by the two weaker pairs of $B^{10}O$ heads, the two sets of pairs interlocking. Plate I (d) shows how in the red, at the other end of the α system, the $B^{10}O$ heads are well separated from the $B^{11}O$ heads, being displaced toward lower frequencies. Plate II shows some of the α heads nearer the origin, in the green; here the A heads $B^{10}O$ cannot be seen, but the presence of the B heads is evident, although their exact positions are masked by $B^{11}O$ structure lines.

The largeness of the separations between corresponding bands of the two isotopes (Table I and II) is notable. Thus for the $(4\rightarrow 0)$ band near the extreme ultraviolet end of the β system, the wave number difference $[\nu(B^{10}O)-\nu B^{11}O]$ is $(\nu_2-\nu_1)=+129$, while $\Delta\lambda=-5.6$, from $\lambda 2091$. At the other end of the β system, the separation for the $(3\rightarrow 10)$ band is $(\nu_2-\nu_1)=-370$, while $\Delta\lambda=+44.4$, from $\lambda 3442$. In the α system, the largest measured separation on the ultraviolet side was $(\nu_2-\nu_1)=+174$, with $\Delta\lambda=-18.4$ at $\lambda 3263$, for the $(6\rightarrow 0)$ band. On the infra-red side, the largest certainly measured separation was $(\nu_2-\nu_1)=-281$, with $\Delta\lambda=$

[10] F. W. Loomis, Astrophys. J. **52**, 248 (1920); A. Kratzer, Zeit. f. Phys. **3**, 460 (1920)

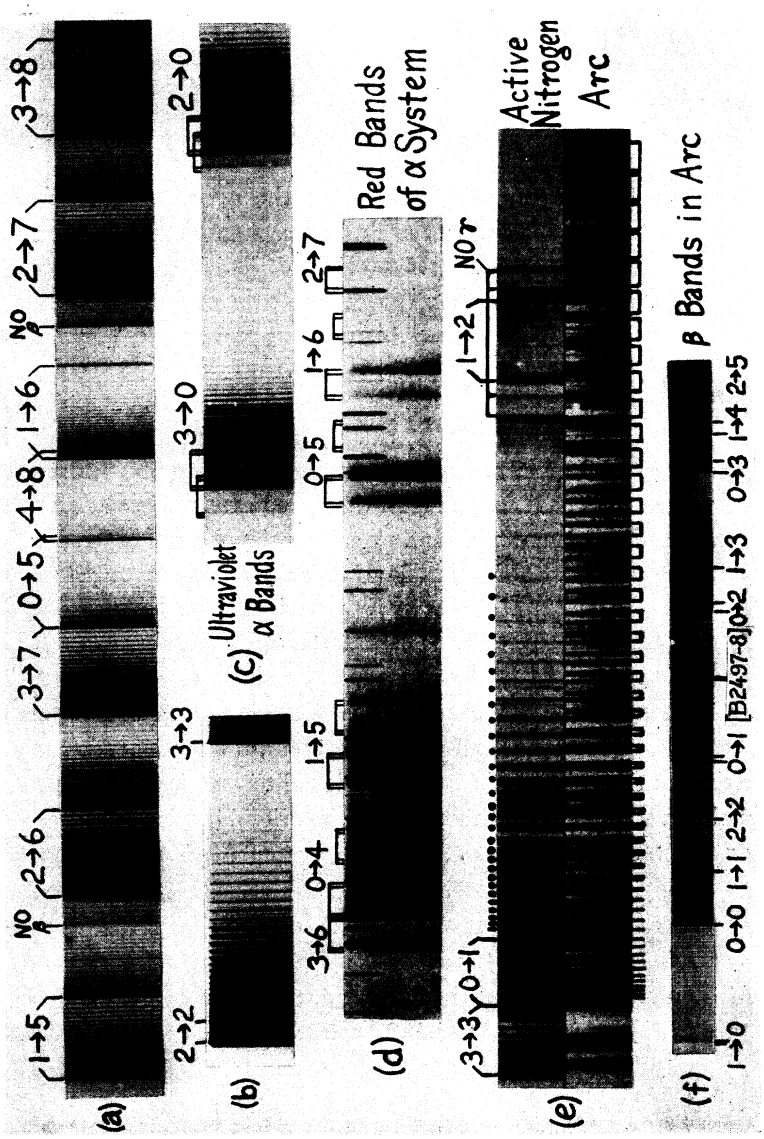

Plate I. *Enlargements of boron monoxide bands.*

DESCRIPTION OF PLATE I

In all cases the $B^{10}O$ heads and structure lines are *weaker* than the corresponding $B^{11}O$ heads and lines. *All* the BO α and β heads are shaded toward the red.

(*a*) Region λ2850-3120, showing heads and structure lines for bands of both isotopes, and isolated positive branch character. The two heads marked NO β are two of the "β bands of active nitrogen" (probably due to NO); they are shaded toward the red.

(*b*) (2→2) β bands, showing weak $B^{10}O$ structure lines among strong $B^{11}O$ lines.

(*c*) Region λ3650-3900, showing α bands on high-frequency side of origin; each band has four heads (A_1, A_2, B_1, and B_2 in order) for each isotope.

(*d*) Region λ5950-7550, showing α bands far on low-frequency side of origin, with $B^{10}O$ heads well separated from those of $B^{11}O$ (too weak to show in 3→6 and 2→7). Comparison, neon plus argon. Some unmarked heads are present due to N_2 (α bands of active nitrogen).

(*e*) Comparison of (0→1) β band in arc and active nitrogen (showing also 3→3 and 1→2); greatly enlarged. The $B^{11}O$ arc doublets are marked below; the high-frequency component of each doublet is alone present in the active nitrogen photograph above (in the reproduction, the juxtaposition of corresponding lines in the two sources is somewhat imperfect, especially at a distance from the head). The $B^{10}O$ lines of the 0→1 band in active nitrogen are marked by dots above; many of them can also be identified in the arc, together with their doublet companions in some cases. The four heads marked NO γ, whose structure lines, extending toward the 0→1 head, cause some confusion, belong to one of the "γ bands of active nitrogen" (probably due to NO). In the arc photographs there are several extra lines due to impurities.

(*f*) Region λ2260-2800 in arc, only slightly enlarged, showing overlapping of succeeding bands. The weaker $B^{11}O$ heads, and the $B^{10}O$ heads, are difficult or impossible to identify (contrast (*a*)).

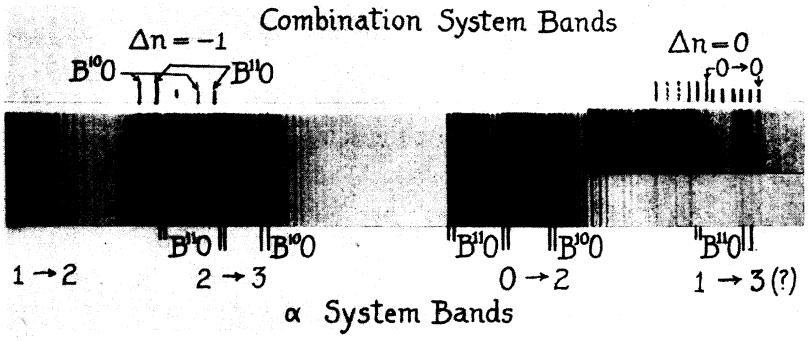

Plate II. Combination system bands, sequences $\Delta n = 0$ and $\Delta n = -1$.—The reproduction is enlarged from a single photograph, except for the insert in the upper right hand corner made from a longer exposure photograph, and showing better the $\Delta n = 0$ sequence. Note the faintness of the combination system bands as compared with the α system bands.—In both systems *A* heads are indicated with shorter, *B* heads with longer, lines adjacent to the reproduction.—Sequence $\Delta n = 0$. $B^{10}O$ and $B^{11}O$ heads superposed. Right to left—*A* heads 0→0, 1→1, 2→2, 3→3, 4→4, 5→5; then *B* heads 0→0, 1→1, 2→2, ... 5→5(?).—Sequence $\Delta n = -1$. Right to left,—superposed *A* heads, first of $B^{11}O$, then of $B^{10}O$; possible *P* branch head of *B* sequence of $B^{11}O$; superposed *B* heads, first of $B^{11}O$, then of $B^{10}O$.

+161A, for the (2→7) band. For the last $B^{11}O$ head measured, in the (2→8) band, the calculated separation is $\Delta\nu = -342$, $\Delta\lambda = +250$A.

In agreement with Aston's results, no indication was found of any other isotope of boron than those of atomic weights 10 and 11.

New Measurements

The experimental methods were much the same as those of Jevons. BCl_3 vapor was led into active nitrogen just as the latter left the exciting discharge tube and entered the afterglow tube, and the resulting spectrum of BO was observed through a quartz window. The BCl_3 used was pure material kindly supplied by Prof. G. P. Baxter, which was some remaining from the recent work by Prof. Baxter and Dr. A. Scott on the atomic weight of boron.[6] This was evidently free from CCl_4, since (in contrast to Jevons' experience) the strongest CN bands were hardly visible on the photographs.[11] In activating the nitrogen, a high-potential discharge from a $\frac{1}{2}$kw, type E, Clapp-Eastham transformer was used, with two large Leyden jars in the circuit. The nitrogen was used at the rate of about 50 liters (at atmospheric pressure) per hour. A pure grade of commercial nitrogen was found satisfactory, in one case without further treatment. Further details are to be found in the later section on direct experimental evidence as to the (BO or BN) origin of the bands. (See also Jevons' paper[4]).

The use of active nitrogen in producing the BO bands has pronounced advantages. Of particular importance is the fact that the heads are sharp and not badly overrun by structure lines from preceding heads; this is due to the low temperature. At the same time, the band systems are very well developed, in spite of the low temperature. Also, the spectrum is particularly free from continuous background and impurities (except for some trouble with the strongest active nitrogen bands). The intensity, however, is only moderate. In the arc, the intensity is much greater, but the advantages that go with low temperature are lost, so that it is difficult to pick out any but the strongest of the $B^{11}O$ heads, while very few of the $B^{10}O$ heads can be identified at all (cf. Plate I (f) with (a)).

For the ultraviolet, photographs were taken with a Hilger type C quartz spectrograph; the dispersion varied from about 4 A/mm at λ2100 to 35 A/mm at λ4000. A smaller quartz spectrograph was used to examine the region below λ2100. For the visible and near infra-red a

[11] This was in spite of the fact that the BCl_3 vapor was allowed to pass through a greased stopcock (the grease was slowly attacked).

Hilger glass spectrograph was used, with a dispersion varying from about 12 A/mm at λ4000 to 100 A/mm at λ6500. For the extreme red and infra-red, dicyanin-stained plates were used, and by exposures of a number of hours the bands were followed to λ8500. For some of the very strong α bands in the visible, brief exposures were sufficient, but for many weaker bands, especially those in the ultraviolet β system, exposures up to several hours were used. In order to render the measurements precise, the best possible focus and a very narrow slit were used, as well as fine-grained plates. The comparison spectra used were the iron arc for most of the ultraviolet, the copper arc at the extreme ultraviolet end, and helium, neon, and argon lines for the infra-red and visible. The correctness of the placing of the comparison lines was checked by measurements on two or more plates. Every effort was made to get as precise data as possible with the instruments used. For this reason and because of internal consistency, it is believed that the results are on the whole more precise than those of Jevons, at least in the ultraviolet. The dispersion used was somewhat less favorable, especially in the visible. Particular care was taken in the identification of the heads, which in some cases are easy to confuse with structure lines. In several cases apparent errors in Jevons' data were corrected; in cases of disagreement special care was taken to check the result. In connection with a study of intensity distribution among the bands, it was attempted to determine definitely the presence or absence of all possible bands.

The results of the measurements are recorded in Tables I and II. From the figures in the J-M column it will be noted that, apart from occasional differences, there is a systematic displacement of 1 to 5 (mostly 2 to 3) wave-number units toward the red in the present data as compared with Jevons'. In the α system, the magnitude of this difference is about inversely proportional to the dispersion. The measurement of band-heads is notoriously uncertain, and the systematic displacement is in all probability due to a difference in method of setting on the heads.[12] In the present measurements, the setting was made on the most intense part of the head, thus treating the latter as if it were a single line. If Jevons' settings were made on the *edge* of each head, which is toward higher frequencies, the difference would be explained. Of course neither procedure is theoretically correct, and the true position of the head should lie between the two, since the true wave-number of the head should be that

[12] That it is not due to displaced comparisons in either Jevons' or the writer's measurements is fairly well shown by its consistency throughout the spectrum, for measurements on several plates. It is certainly not due to displaced comparisons in the present measurements.

of the center of the line of highest frequency (since all the bands are shaded toward the red) in the band, as revealed under high dispersion. Under low dispersion, this blends with neighboring lines, so that the *intensity maximum* would be too far toward the red, by an amount which should vary somewhat with the intensity and dispersion, while the *high-frequency edge* of the blend must obviously be too far in the other direction, by an amount obviously depending on the intensity and the dispersion.

The present very complete measurements on the BO heads are suited for a quantitative test of the vibrational isotope effect. The small more or less constant error presumably present due to the necessary inaccuracy of the settings on the heads should not appreciably affect the determination of the coefficients. Measurements on origins would of course have been preferable, but in view of the difficulty in locating these, involving the use of much higher dispersion and correspondingly reduced intensity, this was impracticable. A detailed analysis of some of the strongest bands, with the use of higher dispersion, is contemplated in the near future.

TABLE I

Bands of the β System

Vibr. quantum nos.		$B^{11}O$ heads					$B^{10}O$ heads				
n'	n''	Int.	λ(I. A)	Wave-no.	C-O	J-M	Int.	λ(I. A)	Wave-no.	C-O	J-M
5	0	00?	.....	[48975.3]	..		000?	.....	[49137.0]	..	
6	1	00?	.....	[48272.2]	..		000?	.....	[48410.5]	..	
4	0	1^+	.....	[47796.5]	..		0	.....	[47926.3]	..	
5	1	1	2121.80	47114.8	−1		0	2117.04	47220.8	0	
3	0	3	2145.37	46597.2	0	2	1	2140.93	46693.8	1	3
4	1	2	2176.32	45934.7	0	1	1^-	2172.80	46009.1	1	2
2	0	4	2202.97	45379.0	0	2	2	2199.92	45441.9	0	2
3	1	4	2234.65	44735.8	0	3	2	2232.55	44777.7	1	3
1	0	6	2264.76	44141.1	−1	3	4	2263.33	44169.0	0	2
2	1	3	2297.21	43517.7	0	(4)	1^+	2296.74	43526.6	0	(−5)
5	3	—	On $B^{10}O$	[43460.9]	−4		2	2299.98	43465.3	−1	2
3	2	6	2330.44	42897.0	1	5	1	2330.96	42887.6	1	
0	0	7	2331.33	42880.8	0	4	*2^+	2331.83	42871.5	3	
4	3	1?	2364.10	42286.6	−4	(−2)				1	
1	1	8	2364.54	42279.7	−1	(5)	*3^+	2365.97	42253.1	0	
2	2	10	2398.53	41679.6	0	4	*6	2401.00	41636.6	−1	
3	3	6	2433.34	41083.2	1	3	—	On (0,1)	[41023.1]	(3)	
0	1	+10	2437.10	41019.9	0	3	*5	2440.71	40959.2	0	
1	2	5	2472.00	40440.8	0		*2^+	2476.67	40364.6	−1	
5	5	2	2505.33	39903.0	0	1	—	Masked	[39809.3]	—	
2	3	6	2507.67	39865.5	0	3	*4	2513.61	39771.4	0	4
6	6	2^-	2542.40	39321.2	−4	(0)	—	Masked	[39208.5]	—	
3	4	7^+	2544.25	39292.5	1	3	—	On (0,2)	[39183.3]	(1)	
0	2	+9	2551.40	39182.4	0	4	6	2568.75	39069.8	0	0
4	5	4	2581.63	38723.6	1	0	*2?	2590.13	38596.7	3	
1	3	8	2588.01	38628.3	−1	2	4	2596.62	38500.1	−2	7
5	6	*2	2619.78	38159.9	0	−8	—	Masked	[38019.7]	—	
2	4	6	2625.64	38074.7	0	3	2^+	2635.43	37933.3	−2	−3

TABLE I—continued

Vibr. quant. nos.		$B^{11}O$ heads					$B^{10}O$ Heads				
n'	n''	Int.	λ(I. A)	Wave-no.	C-O	J-M	Int.	λ(I. A)	Wave-no.	C-O	J-M
3	5	4	2664.09	37525.2	1	2	—	On (0,3)	[37368.8]	(0)	
0	3	+8	2675.27	37368.4	0	1	4	2687.02	37204.9	0	2
4	6	4	2703.37	36979.9	2	1	*2	2715.71	36811.9	−2	
1	4	10	2713.81	36837.7	−1	3	5	2726.91	36660.7	−2	0
5	7	2	2743.42	36440.1	0	−1	*1	Masked	[36255.5]	—	
2	5	9	2753.38	36308.3	0	3	7	2767.86	36118.3	−1	2
6	8	*2?	2784.35	35904.5	−3				[34614.7]		
3	6	7	2793.87	35782.1	1	2	—	On (0,4)	[35579.6]	(2)	
0	4	+8	2809.90	35578.0	1	3	2	2826.86	35364.5	1	1
1	5	8	2850.56	35070.5	0	3	3	2878.97	34845.5	−1	2
5	8	*2+	2877.38	34743.7	0	0	—	Masked	[34516.4]	—	
2	6	10	2892.23	34565.3	0	4	7	2912.17	34328.6	0	2
6	9	*3?	2920.01	34236.5	−8				[34000.5]		
3	7	9	2934.90	34062.7	1	2	—	On (0,5)	[33815.8]	—	
0	5	+6	2956.56	33813.3	−1	3	1	2979.56	33552.2	−1	
4	8	6	2978.47	33564.5	1	2	2	3001.56	33306.4	1	
1	6	7	2999.67	33327.3	0	2	3	3024.22	33056.8	−1	1
2	7	9	3043.64	32845.9	0	2	5−	3069.93	32564.6	0	1
3	8	9	3088.63	32367.5	1	1	3	3116.70	32076.0	2	(−3)
0	6	*1?	3117.35	32069.3	0	4	*2?	3147.46	31762.5	1	−6
4	9	6+	3134.59	31892.8	1	4	3+	3164.33	31593.2	1	
1	7	4+	3162.79	31608.6	0	3	2	3194.62	31293.6	−1	(−16)
5	10	4	3181.34	31424.2	−2	1	—	Masked	[31114.8]	—	
2	8	7	3209.32	31150.3	0	3	4	3243.22	30824.7	2	(15)
6	11	*2?	3228.91	30961.3	−7		1?	3263.25	30635.5	−4	
3	9	9	3256.94	30694.8	1	5	4	3292.75	30361.1	3	(21)
4	10	8	3305.43	30244.6	1	(22)	4−	3343.06	29904.1	2	
5	11	5?	3354.62	29801.1	−4	(12)			[29451.8]		
2	9	*5	3391.22	29479.5	−1		1−	3434.09	29111.5	2	
3	10	6	3441.61	29047.9	0	(−8)	4	3485.97	28678.3	−2	
4	11	4+	3493.06	28620.0	0		—	Masked	[28242.9]	—	
3	11	1	3645.65	27422.1	1				[27013.8]		
4	12	—	Masked?	[27018.5]	—						

Notes for Table 1. The vibrational quantum numbers given should probably all be increased by ½ (see text), but this ½ is conveniently omitted in the table.—Bands not previously measured are indicated by blanks in the J-M column. This column gives in whole wave-number units differences between wave-numbers as measured by Jevons and by the writer. Parentheses around values in this column indicate doubt as to whether the head measured by Jevons was the same as that measured by the writer, or indicate bands probably measured but not identified by Jevons.—The calculated values used for the column C-O (calculated minus observed) were obtained from Eq. (2).—Wave-numbers in brackets are calculated values inserted where measurements were not obtained.—A+? following an intensity value indicates doubt as to the *identity* of the measured head; this usually applies to weak heads among heavy structure lines. A++ preceding an intensity value indicates that the intensity given really applies to two superposed heads. Heads marked "masked" were heavily concealed by structure lines from a preceding head, so that they could not be measured, although in some cases they were identified. Heads marked "On (−,−)" were so close to a head (−,−) that the two were not distinguishable.—Heads not recorded in the table are definitely absent or exceedingly weak.—Additional unidentified heads (or lines), all of intensity 2, were found at $\nu = 33{,}051.1$, 33,003.5, 29891.1, and 28,944.9.

* The head in question is superposed on a structure line so that its estimated intensity is too high and its measured position may be slightly more in error than usual.

TABLE II

Bands of the α System

Vibr. quant. nos. n' n''	Head	$B^{11}O$ heads					$B^{10}O$ heads				
		Int.	λ(I. A)	Wave-no.	C-O	J-M	Int.	λ(I. A)	Wave-no.	C-O	J-M
8 0	A_1		(Possibly	[32966]	—						
	A_2		present)	[32953]	—						
	B_1			[32840]	—						
	B_2			[32827]	—						
7 0	A_1	1	3136.1	31878	0			Faintly			
	A_2	2	3137.0	31869	−4			visible			
	B_1	*2	3148.6	31751	0						
	B_2	*2	3149.7	31740	−2						
8 1	A_1	—	Masked	[31105]	—						
	A_2	—	by NO	[31092]	—			Masked			
	B_1	1?	3226.6	30983	−4			by NO_β			
	B_2	*2?	3227.8	30972	−7						
6 0	A_1	2^+	3249.4	30766	1		—	Masked	[30944]	—	
	A_2	2	3250.6	30755	−1		—	by (8,1)	[30931]	—	
	B_1	2^+	3262.8	30640	1		*2?	3244.4	30813	5	
	B_2	2^-	3264.2	30627	1		*2	3245.6	30802	3	
7 1	A_1	1	3330.2	30019	−3			Very			
	A_2	2	3331.8	30006	−3			faint			
	B_1	2^+	3344.5	29891	−2			or in-			
	B_2	3	3346.2	29876	0			visible			
5 0	A_1	2	3373.2	29637	−1	4	—	Masked	[29788]	—	
	A_2	5	3374.7	29624	−1	4	—	by (5,11)$_\beta$	[29774]	—	
	B_1	7	3387.6	29510	−1	(13)	3?	3370.5	29660	1	(12)
	B_2	5	3389.1	29498	−1	(13)	*2?	3372.1	29647	1	
6 1	A_1	1	3458.9	28903	3		—	Masked	[29030]	—	
	A_2	2	3460.5	28889	3	(−3)	—	by (5,0)	[29017]	—	
	B_1	2	3473.8	28779	1		—	and (3,10)$_\beta$	[28904]	—	
	B_2	3	3475.3	28766	0	(−6)	—	etc.	[28891]	—	
4 0	A_1	5	3510.0	28482	2	3	1^-	3494.7	28607	0	
	A_2	6	3511.3	28472	−1	−1	2	3495.9	28596	−2	(0)
	B_1	7	3525.5	28356	1	(12)	—	Masked	[28481]	—	
	B_2	7	3526.8	28346	−2	(8)	—	by $B^{11}O$, A	[28468]	—	
5 1	A_1	1^-	3599.6	27773	1			Weak,			
	A_2	1	3601.3	27760	1			masked			
	B_1	1	3615.8	27648	0			by NO_β			
	B_2	1^+	3617.2	27638	−3			and (4,0)			
3 0	A_1	5	3660.8	27309	1	5	1	3648.2	27403	0	
	A_2	6	3662.3	27297	−1	2	2	3649.7	27392	−1	
	B_1	8	3677.8	27182	1	4	5	3664.9	27278	−1	
	B_2	10	3679.1	27173	−2		5	3666.6	27265	−1	
6 2		Weak, masked by (3,0), or absent									
4 1		Very weak, masked by (3,0), absent									
2 0	A_1	6?	3828.3	26114	1		1^+	3819.4	26175	2	
	A_2	8	3830.2	26101	0		3	3821.2	26163	1	
	B_1	9	3847.0	25987	2	1	3	3837.5	26051	−1	
	B_2	10	3848.7	25976	0	1	—	Masked	[26037]	—	

TABLE II—continued

Vibr. quant. nos. n'	n''	Head	$B^{11}O$ heads Int.	λ(I. A)	Wave-no.	C-O	J-M	$B^{10}O$ heads Int.	λ(I. A)	Wave-no.	C-O	J-M
5	2		Weak, masked by (2,0), or absent									
3	1	A_1	1?	3928.4	25448	0						
		A_2	2?	3930.3	25436	−1			Masked			
		B_1	3	3948.3	25320	2			by (2,0)			
		B_2	4	3950.5	25306	3						
6	3	A_1	*2?	3959.1	25251	2						
		A_2	*2?	3960.8	25240	−1			Masked			
		B_1	2	3979.5	25122	5						
		B_2	*3	3981.9	25106	7						
1	0	A_1	5	4015.1	24899	0	3	1	4010.5	24927	−1	
		A_2	6	4017.1	24887	−1	2	1	4012.8	24913	−1	
		B_1	7	4035.5	24773	−1	3	*3^+	4031.4	24798	2	
		B_2	8	4037.4	24761	−2	3	3^-	4033.3	24787	0	
4	2	A_1	1?	4033.9	24783	1						
		A_2	—	Masked	[24770]	—			Masked			
		B_1	*3?	4054.7	24656	2			by (1,0)			
		B_2	*2?	4057.0	24642	2						
2	1	A_1	2	4121.9	24254	0	2	1	4120.6	24262	0	
		A_2	4	4124.1	24241	−1	3	2	4122.9	24248	1	
		B_1	6	4143.4	24128	−1	2	*1?	4141.9	24137	−1	
		B_2	7	4145.5	24116	−2	2	2?	4144.2	24123	−1	
5	3		Very weak, masked by (2,1), or absent									
0	0	A_1	2	4225.0	23662	0	2	1^-	4226.3	23655	−3	
		A_2	4	4227.5	23648	0	2	*3?	4229.3	23638	1	
		B_1	4?	4247.9	23534	1	(9)	*5?	4249.4	23526	0	(3)
		B_2	5?	4250.4	23521	1	(8)	4?	4251.9	23512	1	
3	2	A_1	*3	4234.4	23609	1						
		A_2	2	4236.5	23598	−1			Masked			
		B_1	*4?	4257.4	23482	2			by (0, 0)			
		B_2	*4?	4259.5	23470	0			and by $B^{11}O$,(3,2)			
1	1	A_1	8	4339.6	23037	0	4					
		A_2	8	4342.0	23024	0	4		Masked			
		B_1	10	4363.4	22911	0	9		by $B^{11}O$			
		B_2	8	4365.9	22898	0						
4	3		Very weak, masked by (1,1), or absent									
2	2		Apparently absent									
5	4	A_1	1^-	4476.7	22331	−1		—	Obviously			
		A_2	1^-	4479.2	22319	−2		—	present,			
		B_1	2^+	4502.3	22205	−1		—	but			
		B_2	2^+	4504.7	22193	−2		—	masked by $B^{11}O$			
0	1	A_1	7	4586.0	21799	1	3	*2	4600.0	21733	5	
		A_2	8	4588.8	21786	1	3	*5	4602.0	21724	1	
		B_1	10^+	4612.7	21673	0	4	*7	4626.0	21611	0	
		B_2	10^+	4615.4	21661	0	2	*5	4627.9	21602	−4	

TABLE II—continued

Vibr. quant. nos. n'	n''	Head	$B^{11}O$ heads Int.	λ(I. A)	Wave-no.	C-O	J-M	$B^{10}O$ heads Int.	λ(I. A)	Wave-no.	C-O	J-M
3	3		Very weak, masked by (0,1), or absent									
1	2	A_1	5	4715.6	21200	−1	2	—	Masked	[21121]	—	
		A_2	5	4718.7	21186	−1	3	5?	4736.8	21105	3	
		B_1	8	4744.0	21074	−1	4	5?	4761.7	20995	0	
		B_2	8	4746.9	21060	−1	4	5?	4765.0	20980	−1	
2	3	A_1	1^-	4852.8	20601	0		—	Masked	[20506]	—	
		A_2	1^+	4855.7	20589	−2	2	—	"	[20493]	—	
		B_1	2	4882.9	20474	0		*2	4904.8	20382	−3	
		B_2	3	4885.7	20462	−1	2	1^+	4909.1	20364	2	
0	2	A_1	2	5008.0	19962	0	3	—		[19848]		
		A_2	4^-	5011.6	19948	0	3	—	Masked	[19834]		
		B_1	*9	5040.1	19835	0	4	—	by $B^{11}O$	[19722]		
		B_2	6	5043.5	19822	0	4	—		[19708]		
1	3	A_1	0?	5158.8	19379	5						
		A_2	0?	5161.1	19370	1						
		B_1	2^-?	5189.3	19265	−7						
		B_2	1?	5195.5	19242	3						
4	5		Possibly very weakly present									
2	4	A_1	0	5315.1	18809	0	5	—	Masked	[18665]	—	
		A_2	1	5319.0	18795	0	6	—	by $B^{11}O$	[18651]	—	
		B_1	2^+	5351.1	18683	0	5	1	5393.2	18537	2	
		B_2	3	5354.6	18670	−1	6	1	5397.1	18523	2	
3	5	A_1	1^-	5481.1	18240	−2						
		A_2	1	5485.6	18224	−4			Masked			
		B_1		Masked	[18110]	—			by (0,3)			
		B_2		by (0,3)	[18096]	—						
0	3	A_1	3	5508.8	18148	−1	4	—	Masked	[17982]	—	
		A_2	5	5513.0	18134	0	4	—	by $B^{11}O$	[17968]	—	
		B_1	7	5547.5	18021	0	5	3	5599.0	17856	0	
		B_2	8	5551.5	18008	−1	5	5	5603.7	17840	2	
1	4	A_1	2^-	5681.9	17595	−2	3	—	Masked	[17414]	—	
		A_2	2^-	5687.1	17579	1	5	—	by $B^{11}O$	[17401]	—	
		B_1	3^-	5723.1	17468	−2	5	2	5781.6	17291	−3	
		B_2	3^-	5727.4	17455	−2	6	2	5787.6	17274	1	
2	5	A_1	00?	5866.5	17041	0			Masked			
		A_2	0	5872.2	17025	3			by N_2			
		B_1	0	5910.9	16916	−1						
		B_2	0	5916.0	16898	4						
3	6	A_1	00	6062.1	16491	0						
		A_2	0	6067.5	16477	1			Masked			
		B_1	0	6107.6	16368	−4			by (0,4)			
		B_2	— On (0,4)A_1		[16352]	—						

TABLE II—continued

Vibr. quant. nos. n'	n''	Head	$B^{11}O$ heads Int.	λ(I. A)	Wave-no.	C-O	J-M	$B^{10}O$ heads Int.	λ(I. A)	Wave-no.	C-O	J-M
0	4	A_1	3	6113.1	16354	2	7	—	Masked	[16140]	—	
		A_2	3	6118.2	16340	2	6	—	by $B^{11}O$	[16127]	—	
		B_1	5	6159.7	16230	−1	5	2	6242.2	16016	−2	
		B_2	5	6165.4	16215	1	5	2	6248.2	16000	1	
1	5	A_1	2	6317.1	15826	−1	3	1	6409.4	15598	−1	
		A_2	3	6323.5	15810	2	5	1	6414.1	15586	−2	
		B_1	5	6368.5	15698	1	8	2	6460.3	15475	−4	
		B_2	5	6374.8	15682	3	8	2	6467.2	15458	−1	
2	6	A_1	00	6538.0	15291	5			Very			
		A_2	00	6543.0	15279	4			weak,			
		B_1	0	6590.0	15170	0			masked			
		B_2	0	6596.3	15156	1			by N_2, etc.			
0	5	A_1	0	6854.2	14586	2		0	6977.6	14328	−4	
		A_2	1	6861.8	14569	5		0	6986.2	14310	0	
		B_1	2	6913.5	14460	−1		1	7041.4	14198	−1	
		B_2	3	6921.5	14444	4		1	7049.2	14182	2	
1	6	A_1	0	7098.9	14083	−3		00	7240.7	13807	−2	
		A_2	1	7108.0	14065	2		00	7251.0	13788	−4	
		B_1	1	7163.6	13956	−2		0	7307.8	13680	−2	
		B_2	2	7173.2	13937	4		1	7316.8	13663	2	
2	7	A_1	00	7362.3	13579	−4						
		A_2	0	7373.8	13558	4		00	7528	13281	0	
		B_1	0	7434.8	13446	2						
		B_2	1?	7441.8	13434	1		00?	7600	13154	−1	
0	6	A	00	7790	12833	3		000?	7977	12532	−8	
		B	0	7870	12703	6		—		[12398]		
1	7	A	00	8093	12353	−1		000?	8319	12017	12	
		B	0	8174	12230	−5		—		[11904]		
2	8	A	000	8419	11875	−3		—		[11532]	—	
		B	000	8519	11735	11		—		[11406]	—	

Notes:—The notes of Table I in general apply here. The calculated values for the C-O column are from Eq. (1).—The masking of heads by structure lines from a preceding strong head is much more frequent in the α than in the β system; there is also some interference near the long wave-length end by N_2 1st positive bands (α bands of active nitrogen).—The recorded intensities here lack much in value because of the varying sensitivity of the plates used to cover the range. The estimated intensities of the bands in the infra-red are probably relatively too low; and a considerable extension of the α system into the infra-red, very likely to the (2,10) bands near λ 12000, might be expected if the plate sensitivity could be maintained.

QUANTITATIVE CONFIRMATION OF VIBRATIONAL ISOTOPE EFFECT

The following equations represent within experimental error the measured positions of all the heads in Tables I and II, assuming, as is customary, that the minimum values of n' and n'' are zero.

$$\begin{aligned} B^{10}O{:}\nu_a &= \left\{\begin{matrix}23{,}652.2;23{,}638.9;\\ 23{,}526.0;23{,}512.7\end{matrix}\right\} +1285.6n' -11.7n'^2 \quad -1926.8n'' +12.21n''^2 \\ B^{11}O{.}\nu_a &= \left\{\begin{matrix}23{,}661.6;23{,}648.3;\\ 23{,}535.4;23{,}522.1\end{matrix}\right\} +1247.9n' -10.6n'^2 \quad -1873.2n'' +11.68n''^2 \\ \text{Ratio:}\quad &(\text{difference} = -9.4) \qquad 1.0302 \qquad 1.104 \qquad 1.0286 \qquad 1.045 \end{aligned} \tag{1}$$

$$\begin{aligned} B^{10}O{:}\nu_\beta &= 42{,}874.6 - 0.19n'n'' \quad +1304.6n' -10.43n'^2 \quad -1927.9n'' +12.66n''^2 \\ B^{11}O{:}\nu_\beta &= 42{,}880.9 - 0.17n'n'' \quad +1268.8n' -9.98n'^2 \quad 1872.9n'' \quad +11.84n''^2 \\ \text{Ratio:}\quad &(\text{difference} = -6.3) \qquad 1.0282 \qquad 1.045 \qquad 1.0294 \qquad 1.069 \end{aligned} \tag{2}$$

These were obtained independently for the α and β systems of each isotope.[13,14] In determining the coefficients of n' and n'' for the α system of each isotope, the average measured wave-number for the four α heads was used. This was justifiable, since the mutual separations of the four heads appear to be constant within experimental error. This latter conclusion was also reached by Jevons, although the measured separations here obtained differ slightly from his results. The intervals between the four heads are the same within experimental error for both isotopes. This is to be expected since the four heads are presumably due to a multiple electronic level [(I) p. 123], and since no appreciable electronic isotope effect, and certainly no differential effect between the different sub-levels, is to be expected [(I) p. 124].

The $n'n''$ terms of Eq. (2) arise from the fact that the measurements are on heads instead of on band-origins, and are due to the variation with n' and n'' of the distance from origin to head. All the other coefficients, as well as the constant term, also necessarily contain relatively small contributions from this source [cf. (1), Eqs. (20), (20′) of ref. 29, and (21)]. Except for these small contributions, the ratios for the two isotopes of corresponding coefficients of n' and of n'' should give experimental values of ρ, and the ratios for the coefficients of n'^2 and n''^2 should give experimental values of ρ^2 [see (I), Eq. following (13)]. The experimental ratios are given above in connection with Eqs. (1) and (2). It is possible to state, from an approximate determination of the magnitudes of the small head contributions (see later section), that these produce an error of not

[13] Applying the combination principle, the energy term was determined for each vibrational level. This unexpectedly revealed the $n'n''$ terms of Eq. (2). It would also reveal any irregularities (perturbations) in the spacing of the energy levels, but none was found within experimental error.

[14] Eq. (2) was formulated without attaching much weight to the data for $n'=6$, for which the identity of the heads was uncertain. A positive cubic term would, however, make possible a considerable improvement in the difference" calc.−obs." for the $n'=6$ bands, and a decided improvement for the $n'=5$ bands, and should probably be included.

more than 1 unit in the last figure in these ratios as given above. Hence the latter may be accepted as correct within experimental error. The question of the constant terms will be discussed later.

Attention may conveniently be drawn at this point to the very close agreement of the coefficients of n'' and n''^2 in the α and β systems; the less good agreement for $B^{10}O$ than for $B^{11}O$ may be ascribed to the relative lack of reliable data, especially in the α system, due to masking of $B^{10}O$ heads by strong $B^{11}O$ structure lines. The agreement for $B^{11}O$ is such as to show practically without question that the α and β systems have their final state in common. This is confirmed (see below) by the existence of a combination system.

From Eqs. (1) and (2) the weighted mean values of the ratios are 1.0291 ± 0.0003 for ρ and 1.062 ± 0.008 for ρ^2.[15] Comparing these with the theoretical values $\rho = 1.0292$ and $\rho^2 = 1.0593$ for BO, $\rho = 1.0276$ and $\rho^2 = 1.0560$ for BN, it will be seen that the experimental result for ρ is in extremely good agreement for BO, and in disagreement for BN by an amount far beyond the probable error in the experimental value. The comparison is also favorable to BO in the case of the mean quadratic term ratio, although this result is not at all decisive.

In the preceding it has been tacitly assumed that the choice lay only between BO and BN. The arguments used above in favor of BO against BN also apply against any other diatomic boron compound; in addition the direct evidence (see below) definitely excludes any compound other than an oxide or nitride. The diatomic character of the emitter is attested, according to the quantum theory of band spectra, by the simple structure of the α and β systems and bands. The familiar diffuse and ordinarily apparently headless boric oxide bands in the visible are, however, probably due to a complex emitter, which may be assumed, as apparently in the past, to be B_2O_3.

Although the above theoretical evidence in favor of BO is extremely definite and convincing, it is of course necessary to establish the absence of contradictory evidence of a more directly experimental nature.

Chemical Evidence as to the Identity of the Emitter of the Bands

The BO bands were originally ascribed by Jevons to a nitride of boron, presumably the well-known stable white compound BN. This was a natural supposition, since the bands are developed in active nitrogen, and since, according to Jevons, the (white) product deposited on the walls of the

[15] The ratios for the coefficients of n' (α), n' (β), n'' (α), and n'' (β), were given the respective weights 2, 3, 4, and 6, in accordance with the writer's judgment of their relative reliabilities. The *unweighted* means are $\rho = 1.0291 \pm 0.0004$; $\rho^2 = 1.066 \pm 0.010$.

afterglow tube contains combined nitrogen. Again, when $(CH_3)_3BO_3$ was substituted for BCl_3 the bands were developed as before, indicating that *chlorine* was not required for their production. Also they were *not* obtained in the uncondensed discharge through pure BCl_3, indicating the necessity of *some* other element than boron. Jevons concluded that boron and nitrogen alone were necessary. The writer at first accepted this conclusion.[3]

Before considering the experimental evidence for BO, it will be desirable to consider the occurrence of the BO and B_2O_3 bands in various sources. Jevons[4] found the BO bands in the B_2O_3 arc in air; also in the boron arc in air, oxygen, and nitrogen, but weaker in oxygen. This last result appeared to support the nitride origin of the bands, but was admittedly inconclusive, since neither the oxygen nor the nitrogen was entirely pure. Kayser and Konen point out (Handbuch der Spektroscopie, vol. VII, section on boron) that Exner and Haschek had previously obtained the stronger of the β bands in the arc, and Hagenbach and Konen a number of the α bands in the arc, and indications of them in the spark. Apparently these, as well as certain bands obtained by Plücker, Ciamician, and others (see Kayser and Konen, vols. V and VII on boron) by the discharge through BF_3, and some others measured by Kühne, were formerly referred to collectively without distinction as the "boron bands," in contradistinction to the boric oxide bands. The *latter* are particularly prominent in the flame, and also occur in the arc in air, and in the spark under proper conditions. The BO bands are absent in the flame, according to Jevons and others. Probably thermal dissociation of B_2O_3 to yield BO occurs in the arc, but not in the flame. Jevons failed to find the BO bands in the spark in an atmosphere either of oxygen or of nitrogen.

The intensity of the BO bands in relation to the oxygen content of the nitrogen used in generating them by its reaction with BCl_3, gave the first piece of direct experimental evidence in favor of BO as their emitter. In the present work, a cylinder of commercial nitrogen, stated to be 99.6 per cent pure, was first used. This was purified by contact with wet phosphorus, according to the method used by Jevons,[4] and then passed through calcium chloride, soda lime, and phosphorus pentoxide. Under these conditions, the BO bands showed a very pronounced maximum of intensity for a purification period of about 45 minutes. Spectroscopic and visual observations on the afterglow showed that the α and β bands *of active nitrogen* were present in more or less equal intensity at this stage. When the purification period was greatly reduced, the nitrogen α bands became much weaker, the β bands much stronger; when it was increased

to several hours (or days) the α bands became considerably stronger, the β bands much weaker.

Now E. P. Lewis,[16] and also Rayleigh,[17] have shown that the β (and γ) bands of active nitrogen require the presence of oxygen. Rayleigh collected much evidence on the occurrence of these bands in various sources; this evidence points very strongly to NO as their emitter. Lewis had also previously obtained strong evidence of the NO origin of the γ bands, and thought that the β bands might also be due to NO. Recent work indicates[18] that the β and γ bands probably have a common final state, so that there is little doubt that both are due to NO, especially since the structural simplicity of both systems indicates a diatomic emitter in each case. The α bands, however, are due to N_2.

Jevons has suggested,[19] in criticizing the writer's conclusions as to the origin of the BO bands, that the favorable influence of oxygen on their intensity might be due to its known effect (cf. papers by E. P. Lewis, and by Rayleigh and Fowler) in promoting the formation of active nitrogen. The above account evidently disproves this, since, beginning at a stage of purification where the BO bands are at their strongest, the *removal* of oxygen actually increases the yield of active *nitrogen*, as measured by the intensity of its α bands, while greatly decreasing the intensity of the NO and the BO bands. If a stage was reached where there was a lack of oxygen for the catalysis of the formation of active nitrogen, it is probable that the phosphorus vapor which was present fulfilled the same function.

In later experiments with a cylinder of nitrogen stated to be 99.7 per cent pure, but evidently much purer than the first, the oxygen content was already too small for the best results with BO, even when the phosphorus treatment was omitted. In fact, the intensity of the BO bands was markedly increased when a small amount of air was admitted. The behavior of $SiCl_4$ with this nitrogen was in striking contrast to that of BCl_3. Although too pure for maximum BO intensity, it was by far too impure to permit more than a faint indication of the purple glow of the SiN bands. The SiN bands[3] did not reach full intensity until the nitrogen had been purified as far as possible (at least 2 hours). Apparently oxygen destroys or inhibits the formation of SiN.

[16] E. P. Lewis, Astrophys. J. **20,** 49 and 58 (1904); Phil. Mag. **25,** 826 (1913)

[17] Rayleigh, Proc. Roy. Soc. A **93,** 254 (1917). Rayleigh found one objection which seemed to him to make it impossible to ascribe the bands to NO or any oxide of nitrogen. This objection, however, hardly seems vital in the light of present knowledge.

[18] R. T. Birge, Nature, Nov. 1, 1924. The writer had also tentatively reached the same conclusions.

[19] W. Jevons, Nature, May 24 and May 31, 1924; Proc. Roy Soc. A **106,** 174 (1924)

The simultaneous presence, when the BO bands are at their strongest, of active nitrogen and of active[20] or excited NO may be accounted for by a pair of reactions such as the following (the prime denotes an electronically excited molecule):

(A) $BCl_3+N_2' \rightarrow BN$ (or BN')$+NCl_3$; (B) $BN+NO' \rightarrow BO'+N_2$. (3)

Or possibly,

(a) $BCl_3+NO' \rightarrow BO+NCl_3$; (b) $BO+N_2' \rightarrow BO'+N_2$. (3′)

Both pairs of reactions assume that NO′ has not enough energy to form BO′ from BCl_3 in one step. However, the high intensity of the BO bands favors a one-stage reaction, and it may be that the presence of N_2' is not essential. Reaction (A), whether or not involved in the formation of BO′, would account for the presence of nitride nitrogen observed by Jevons in the reaction-product; BN, although thus probably present, apparently does not emit a spectrum. The conclusion recently expressed by Birge[21] that active nitrogen consists of metastable excited nitrogen molecules in the state necessary for the emission of the α bands,[22] affords the simplest explanation of the behavior of active nitrogen in producing chemical reactions and exciting spectra. Its action would thus be analogous to that of excited mercury atoms in the work of Franck and Cario.[23]

The exact mechanism of formation of BO′, although of much interest in itself, is not essential to the present argument, but the above analysis shows that the oxide origin of the bands is reasonable and probable. If the bands were due to BN, the unlikely assumption would be needed that N'_2, although alone capable of producing the SiN bands, is much less effective than NO′ in producing the BN bands.

Noting that the BO′ molecules are formed in a medium consisting largely of inert unexcited nitrogen molecules, with a small proportion of NO and NO′ and doubtless O_2 and other molecules, it is not surprising that the BO spectrum is strong and that of B_2O_3 negligibly weak

[20] Evidence for the existence of active, that is metastable, excited NO is to be found in observations of Lord Rayleigh[17] and of the writer that the bluish glow of the β bands shows an even greater persistence than the yellow glow of the α bands. The fact that in impure active nitrogen the β bands may appear without the α bands also indicates an independent metastable existence.

[21] R. T. Birge, Phys. Rev. **23**, 295 (1924); Nature, Nov. 1, 1924; cf. also M. N. Saha and N. K. Sur, Phil. Mag. **48**, 421 (1924).

[22] The emitting state of active nitrogen can, however, hardly be identical with the metastable state. Presumably the transfer from the latter to the former is accomplished in collisions with other molecules.

[23] Franck and Cario, Zeit. für Physik **9**, 259; **10**, 185; **11**, 161 (1922); **17**, 202 (1923). This suggestion has been made independently by Birge (unpublished), by the writer (Nature, Sept. 6, 1924; also indicated in connection with the Cu halides in Phys. Rev. **23**, 767, 1924), and by Saha and Sur.[21]

or absent. A BO molecule would have to make a very large total number of encounters with other molecules before a molecule of B_2O_3 could result. In order to give the B_2O_3 spectrum, this molecule might also have to make a favorable encounter with an excited N_2 or NO molecule.

Jevons recently brought forward evidence which he considered irreconcilable with the oxide origin of the BO bands. In experiments with the uncondensed discharge through mixtures of oxygen with various chlorides ($TiCl_4$, $SiCl_4$, CCl_4) he uniformly obtained oxide bands. With BCl_3 he obtained the B_2O_3 bands—each of which now showed a series of heads—but not the BO bands. The writer has confirmed this result for the visible region, observing incidentally that the B_2O_3 bands are best brought out with a great excess (80:1 was used) of O_2 over BCl_3 molecules. Although these results do not help the cause of BO, they are after all not wholly surprising. If B_2O_3 and BO molecules are equally easily excited by the discharge, it is necessary only that the number of BO molecules present at any moment shall be negligible compared with the number of B_2O_3 molecules. This may well be the case, in an atmosphere consisting of oxygen atoms and molecules, in view of the chemically highly unsaturated character which BO must have.

Photographs of a carbon arc whose anode contained in various experiments BN, B_6C, or B_2O_3, gave very strong evidence against BN and in favor of BO. The arc was run in a Pyrex bulb which could be evacuated and filled with gas as desired. In the case of all three compounds, the BO β bands always appeared, in moderate intensity, when an atmosphere of air, or oxygen (about 99.7 per cent pure, the rest N_2) was used; but under like conditions, as gauged by the intensity of the boron doublets at λ2497 and λ2089, in pure nitrogen (phosphorus-treated) and in nearly pure nitrogen (containing a little oxygen), they were completely absent. The α bands, and with them the B_2O_3 bands, were similarly present with air or oxygen, but disappeared when nitrogen was used.

HALF-INTEGRAL VIBRATIONAL QUANTUM NUMBERS

In Eq. (1) there is a difference of unexpected magnitude between the constant terms for the α systems of $B^{10}O$ and $B^{11}O$, and similarly in Eq. (2) for the β systems. According to the theory, these constant terms are "electronic" (ν^e terms) except for a small "rotational" contribution due to the use of data on heads. When approximate allowance is made, on the basis of a study of band structure (see below) for the latter, the differences of Eqs. (1) and (2) are slightly *increased* in magnitude, to (-10.1) and (-7.2), respectively. According to the quantum theory of band

spectra as hitherto accepted, these corrected differences should represent *purely electronic* isotope effects. According to the Bohr theory, applicable to an atom with one electron [(I) Eq. (9)], differences of -0.12 and -0.21, respectively, might be expected.[24] The much larger results here observed are absolutely out of harmony with considerations previously presented [(I) pp. 124-5]. Hence any alternative explanation that does not do violence to the theory is greatly to be preferred.

If, in formulating Eqs. (1) and (2), we had assumed the minimum values of n' and n'' to be $1/2$, instead of 0, the linear term coefficients and the constant terms would obviously be somewhat different. The transformation can be effected by replacing n' by $(n'-1/2)$ wherever n' appears in Eqs. (1) and (2), similarly replacing n'' by $(n''-1/2)$, and recasting in the original form of (1) and (2). It can easily be verified that such a transformation alters the corrected differences of corresponding constant terms for $B^{10}O$ and $B^{11}O$, from -10.1 to -2.3 for the α system, and from -7.2 to $+2.4$ for the β system. The electronic isotope effect thus becomes zero in both cases within an amount which can reasonably be attributed to the combined effect of errors in the determination of the constants and coefficients of Eqs. (1) and (2). This result cannot be accomplished by any other assignment of minimum values of n' and n'', if we restrict ourselves to the possibilities 0, $+1/2$, $+1$. Since half-integral values of n' and n'' with a minimum value $+1/2$ are by far more probable than a large electronic isotope effect or other serious failure in the theory, they may be quite definitely accepted—unless one wishes to entertain the possibility of fractional values other than $1/2$. It is hoped that later more accurate measurements will make the evidence more nearly quantitative.

It may be noted (cf. Eqs. (8) and (9) below) that the transformation to half quantum numbers alters the mean experimental value of ρ from 1.0291 to 1.0293. The new value is, however, in just as good agreement as before with the theoretical value 1.0292 for BO; and is slightly worse than before for BN. With very accurate data, the dependence of the experimental ρ on the absolute numbering would furnish an independent check on the latter, additional to that of the previous paragraph.

The existence of half vibrational quantum numbers is in line with recent work in line and band spectra.[25] Several investigators have re-

[24] No isotope effect has as yet been reported in the boron line spectrum. The doublets at λ 2497 and λ 2089 are obviously, from the relative intensity of their components, not of isotopic origin.

[25] The work of Sommerfeld and Landé on the structure and Zeeman effect of multiplets may be cited. A. M. Mosharaffa (Proc. Roy. Soc. A **105**, 641, 1924) has also found half quantum numbers useful in the Stark effect.

cently shown that half-integral rotational quantum numbers are the rule rather than the exception in band spectra.[26] There is also evidence from specific heat data.[27] The situation in the BO molecule—and doubtless in many or perhaps most molecules—may parallel that assumed by Heisenberg in explaining the structure and Zeeman effect in doublets and triplets in line spectra. Thus, for example, in the normal state of the Na atom, the valence electron was assumed to have 1/2 quantum each of radial and of azimuthal motion.[28] Analogously in BO, the vibrational and rotational quantum numbers may both be half-integral, the sum of the two being integral. This would involve a null-point energy of 1/2 quantum each of vibration and rotation.[29]

Structure of BO Bands and Rotational Isotope Effect

Absence of negative branch. A preliminary account of salient features of the structure of the BO bands will be given here, but a more detailed analysis will be reserved until measurements can be made with higher dispersion photographs. All the BO bands are shaded toward the red, so that the head is always on what is presumably a positive branch, capable of representation by an equation of the form $\nu^m = A + Bm + Cm^2$, C here being negative; m is the rotational quantum number. There is no evidence of a null-line: this is probably very close to the head (see below). In only two of the β bands is more than one set of strong lines associated with each head; in the $(2\frac{1}{2} \rightarrow \frac{1}{2})$ and $(4\frac{1}{2} \rightarrow 1\frac{1}{2})$ bands additional lines of a presumably negative branch about 2/3 and 1/3 as intense, respectively, as those of the positive branch, are present. Weak negative branch lines also appear in the $(2\frac{1}{2} \rightarrow 2\frac{1}{2})$, $(1\frac{1}{2} \rightarrow 3\frac{1}{2})$, and $(3\frac{1}{2} \rightarrow 5\frac{1}{2})$ bands.[30] Similar peculiarities probably exist in the α system. Other cases of inequality of intensity of posi-

[26] A. Kratzer, Münch. Ber. p. 107 (1922); Ann. der Phys. **71**, 72 (1923); R. Frerichs, Zeit. f. Phys. **20**, 170 (1923); E. Hulthén, Ann. der Phys. **71**, 41 (1923); E. F. Barker, Astrophys. J. **58**, 201 (1923); W. F. Colby, Astrophys. J. **58**, 303 (1923); etc.

[27] R. C. Tolman (Phys. Rev. **22**, 470, 1923) has shown that the assumption of a null-point energy of 1/2 quantum fits the experimental data for the rotational specific heat of hydrogen just as well as the earlier assumption of a minimum of 1 quantum. The assumption of zero null-point energy definitely does *not* fit the facts. See F. Reiche, Ann. der Phys. **58**, 657 (1919); E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).

[28] W. Heisenberg, Zeit. f. Phys. **8**, 273 (1922)

[29] This may have a bearing on the question of the relative vapor pressures of isotopes; in this connection cf. Lindemann and Aston, Phil. Mag. (6) **37**, 523 (1919), and Lindemann, Phil. Mag. (6) **38**, 173 (1919).

[30] Probable faint traces are present in the $(3\frac{1}{2} \rightarrow \frac{1}{2})$, $(3\frac{1}{2} \rightarrow 5\frac{1}{2})$, $(3\frac{1}{2} \rightarrow 6\frac{1}{2})$, $(2\frac{1}{2} \rightarrow 6\frac{1}{2})$, and doubtful faint traces in the $(4\frac{1}{2} \rightarrow 6\frac{1}{2})$, $(1\frac{1}{2} \rightarrow 5\frac{1}{2})$, $(3\frac{1}{2} \rightarrow 7\frac{1}{2})$, $(2\frac{1}{2} \rightarrow 7\frac{1}{2})$, and $(3\frac{1}{2} \rightarrow 8\frac{1}{2})$ bands. Doubtless in a few additional cases negative branch lines are present which accidentally coincide, at the dispersion used, with the positive branch lines.

tive and negative branches are on record. The usual absence of more than one series of structure lines from each head is well shown in Plate I, especially in (*a*).

Confirmation of rotational isotope effect. Careful measurements were made for both isotopes of all possible lines in the ($\frac{1}{2}\rightarrow 3\frac{1}{2}$), ($2\frac{1}{2}\rightarrow 3\frac{1}{2}$), and ($2\frac{1}{2}\rightarrow 5\frac{1}{2}$) β bands. The lines begin to be resolved at about the fifth from the head, and can be followed to about the 40th from the head. By plotting the first differences between successive lines against successive integers, values of the coefficient C, presumably moderately accurate, were obtained from the average second differences. The results for all three bands (using the half-quantum vibrational numbering) may be expressed by the following pair of equations, the values of $B^{10}O$ being considerably less reliable than for $B^{11}O$.

$$B^{10}O: \quad C_\beta = C_0 - \alpha' n' + \alpha'' n'' = -0.2849 - 0.0204 n' + 0.0175 n''$$

$$B^{11}O: \quad C_\beta = C_0 - \alpha' n' + \alpha'' n'' = -0.2715 - 0.0206 n' + 0.0172 n'' \qquad (4)$$

Ratio of coefficents:				
	(theory)	1.059	1.090	1.090
	(experiment)	1.049	0.99	1.02

The ratios of corresponding coefficients for the two isotopes give an approximate confirmation of the theory [cf. (I), Eqs. (7A), (18), and ref. 28] for the constant part of C; for the coefficients α' and α'' the result is unsatisfactory; the disagreement, however, is probably in all three cases within the limits of experimental error.[31] Another approximate confirmation of the rotational isotope effect has been shown to exist in the case of CuH.[32]

Determination of coefficients of band structure. Assuming only that the lines measured belong to a series (presumably a positive branch) of substantially the usual form $\nu = B' + 2B'm + Cm^2$, where $B' = B_0' - \alpha' n'$, and $C = B' - B'' = C_0 - \alpha' n' + \alpha'' n''$, it is possible from the data of Eq. (4), together with the coefficient of $n'n''$ in Eq. (2), to determine B' and B''.[33] According to (I) ref. 29, Eq. (20′), the coefficient p of $n'n''$ should be equal to $p = [(2B_0'^2/C_0 - 2B_0' + (3B_0'^2/C_0^2 - 4B_0'/C_0)\alpha' n' - (3B_0'^2/C_0^2 - 2B_0'/C_0)\ \alpha'' n'' + \ldots .)]\alpha'\alpha''/C_0^2$. The experimental p may be assumed to correspond to the average values $n' = 2\frac{1}{2}$, $n'' = 3\frac{1}{2}$. Inserting these values in the p equation together with the values of α', α'',

[31] The effect of higher power terms in m should cause an error of 0.001 or 0.002 in C; the relative error from this cause for the two isotopes should be completely negligible.

[32] R. S. Mulliken, Nature, April 5, 1924.

[33] It is *possible* (cf. A. Kratzer, Ann. der Phys. **71**, 72, 1923; Zeit. f. Phys. **23**, 298 1924) that the bands are of a type for which ν is of a somewhat different form.

and C_0 from Eq. (4), and putting $p=-0.17$ according to Eq. (2), one obtains for $B^{11}O$, by successive approximations, $B_0'=2.03$. Then[33] for $B^{11}O$,[34] with a probable error of perhaps 5 per cent,

$$B^{11}O:\ B_\beta'=2.03-0.021n' \text{ and } B_\beta''=B_\beta'-C_\beta=2.30-0.017n''. \quad (5)$$

It may be noted that α' and α'' have the usual sign, and that α', α'', C_0 and the B's, have entirely reasonable numerical values; thus, e.g., in the violet CN bands, $B'=1.96-0.022n'$; $B''=1.89-0.017n''$.

The values of Eq. (5), and corresponding values[34] for $B^{10}O$, can now be used to obtain approximate corrections so as to reduce Eq. (2) to the corresponding equation for a system of band origins, with the help of (I) ref. 29, Eq. (20'). It was in this way that the *corrected* differences, for the constant (ν^e) terms of Eqs. (1) and (2), used in the preceding section, were obtained. This procedure also shows that the heads of the various bands must be very near the origins, the calculated values of m_{head} being between 5 and 12 for most of the bands; it is then not surprising that it is at just about this number of lines from the head that the bands begin to be resolved.

Although no $n'n''$ terms were detected in the measurement of the α heads, use can be made of the fact that the α and β bands have a common final state. Then one may assume $B_\alpha''=2.30-0.017n''$ for $B^{11}O$. Measurements on some of the bands give, assuming the coefficient of n'' from the β system measurements,[35]

$$B^{11}O;\ C_\alpha=-0.38-0.014n'+0.017n'' \quad (6)$$

B_α' can now be calculated, and,

$$B^{11}O:\ B_\alpha'=1.92-0.01n';\ B_\alpha''=2.30-0.017n'' \quad (7)$$

From the data now available, it can be calculated that the coefficient of $n'n''$ for the α system should be -0.04: this small value is in agreement with the failure to detect the coefficient experimentally.

Equations for band origins. From the data now available, it is possible to obtain in place of (1) and (2) the following probably moderately accurate equations for the *origins* of the BO bands, using the half-quantum numbering;

[34] A separate calculation for $B^{10}O$ from the experimental values of p, α', α'', and C_0 would not be very reliable; the theoretical values are $B'=2.15-0.023n'$ and $B''=2.44-0.019n''$.

[35] It is possible that the values of B' and C differ appreciably for the four different α heads. Eq. (6) was determined from measurements on A_2 and B_2 structure lines; there was some indication of a systematic difference between the two, but an average was used for Eq. (6).

$$B^{10}O:\ \nu_\alpha = \left\{\begin{matrix}23{,}960.6;23{,}947.3\\23{,}834.4;23{,}821.1\end{matrix}\right\} + (1298.0n' - 11.7\ n'^2) - (1939.4n'' - 12.19n''^2) \tag{8}$$

$$B^{11}O:\ \nu_\alpha = \left\{\begin{matrix}23{,}962.9;23{,}949.6\\23{,}836.7;23{,}823.4\end{matrix}\right\} + (1259.1n' - 10.6\ n'^2) - (1885.2n'' - 11.66n''^2)$$

Ratio: (Diff. $= -2.3$) 1.0309 1.038 1.0288 1.045

$$B^{10}O:\ \nu_\beta' = 43{,}168.6 + (1316.7n' - 10.53n'^2) - (1941.5n'' - 12.58n''^2)$$
$$B^{11}O:\ \nu_\beta' = 43{,}166.2 + (1280.3n' - 10.07n'^2) - (1885.7n'' - 11.77n''^2) \tag{9}$$

Ratio: (Diff. $= +2.4$) 1.0284 1.046 1.0296 1.069

Each equation is in the form $\nu = \nu^e + \nu^n = (E'^e - E''^e)/h + (E'^n - E''^n)/h$, and so yields values of ν^e, E'^n, and E''^n.

Combination System Bands

In all the photographs of the α system of BO, the $(1\frac{1}{2} \rightarrow 3\frac{1}{2})$ band is obscured by a peculiar structure (see Plate II) which looks like a group of lines or band-heads, some of which appear distinctly shaded toward the violet. Similar peculiarities appear very markedly in the $(2\frac{1}{2} \rightarrow 3\frac{1}{2})$ band, (Plate II), and less prominently near the $(\frac{1}{2} \rightarrow 1\frac{1}{2})$ and $(\frac{1}{2} \rightarrow 3\frac{1}{2})$ bands and on the $(2\frac{1}{2} \rightarrow 5\frac{1}{2})$ band.

These extra lines or heads do not agree in position with any of the B_2O_3, the N_2, or the NO band-heads, nor have they been found in the spectrum of BCl_3.[36] It seemed possible that they might be due to transitions from β system initial states to α system initial states. The positions of the *origins* of such a combination system of bands should obviously be calculable from Eqs. (8) and (9). The result is:

$$B^{10}O:\ \nu = \nu^e + 1316.7n' - 10.53n'^2 - 1298.0n'' + 11.7n''^2 \tag{10}$$
$$B^{11}O:\ \nu = \nu^e + 1280.3n' - 10.07n'^2 - 1259.1n'' + 10.6n''^2$$

Here $\nu^e = 19$, 205.6, 19218.9, 19331.8, and 19345.1, corresponding to the A_1, A_2, B_1, and B_2 α levels.[37] These equations might be expected to give results in error by a few wave-number units, on account of the uncertainties involved in the determination of the coefficients in Eqs. (1) and (2) for the α and β bands, and especially in the corrections subsequently applied in obtaining Eqs. (8) and (9).

From the previously estimated values of B_β' and B_α', one should have for the new bands, for $B^{11}O$, $B' = B_\beta' = 2.03 - 0.021n'$: $C = +0.11 -$

[36] Photographs of the B_2O_3 bands, and data on the bands produced by the discharge through BCl_3, are given by Jevons[19].

[37] The ν^e values directly calculated from Eqs. (8) and (9) are 2.3 less than here for $B^{11}O$ and 2.4 units more for $B^{10}O$. The use of the same mean value here for both isotopes is justified by the likelihood that the apparent discrepancy between the ν^e values of the two isotopes is due to errors in the determination of ν^e in the α and β systems. It may be noted that the directly calculated values give as good (or slightly better) agreement with the data of Table III as the mean values here used.

$0.021n'+0.014n''$. The positive value of C shows that the new bands, unlike the α and β bands, should be shaded toward the violet; the head should be on the negative (P) branch, and on account of the relatively small numerical value of C, at a considerable distance from the origin, -35 wave-number units, for example, in the case of the $\frac{1}{2}\rightarrow\frac{1}{2}$ band. No conspicuous heads were, however, found in the calculated positions. But it was found that practically all the unidentified lines or heads mentioned above could be explained by assuming each to correspond to the beginning of a Q branch. Such a Q branch would have its head at the band-origin, and, with a low value of C, a low-temperature source, and under moderate dispersion, as here, this head might not differ much in appearance from that of a P or R branch. The weakness of the first few lines should, however, cause an apparent small shift toward the violet, giving the appearance of a diffuse line or head shaded toward the violet, as observed. On this basis, assuming a shift of $+3$ units from the origins as calculated from Eq. (10), the agreement between observed and calculated wave-numbers is complete for the transitions $\beta\rightarrow\alpha(A_1)$ and $\beta\rightarrow\alpha(B_1)$, for both isotopes. There is, however, no definite evidence of transitions to the A_2 and B_2 α levels; such transitions, if present, must give less than one tenth the intensity of those to the A_1 and B_1 levels. The transition to B_1 shows greater intensity than that to A_1, except in the $\Delta n=0$ sequence, where the reverse is true. It is possible that R branches are present in the new bands, but escape observation because of the lack of a head. In no case were individual structure lines visible in the new bands, presumably because of insufficient intensity as compared with the background of relatively intense α system bands. All the bands of the new system are very weak as compared with like-numbered α and β bands. In one or two cases there is a suggestion of a P branch; e.g., on the low-frequency side of the B_1 head at 20,609 there is a shaded region beginning at about 20,572 and extending toward the violet (cf. Plate II). The usual absence of P branches in the combination bands may be correlated with their absence in the β (and α?) bands.

In spite of various peculiarities and irregularities noted above, the agreement recorded in Table III is so remarkable as to leave no reasonable doubt that the data really correspond to a system of bands involving a transition from β to α states of BO.[38] For instance, the arrangement of the new bands in sequences is of a very unusual character, entirely in accord with prediction, due to the near-equality of the coefficients of n'

[38] There is of course a possibility that the heads here observed correspond to transitions to some third pair of α levels A_3 and B_3; and the interpretation as Q branches *may* not be correct.

TABLE III

Bands of the Combination System

Vibr. Quant. Nos. n'	n''		$B^{11}O$ Heads Int.	λ(I. A)	Wave-no.	C-O	$B^{10}O$ Heads Int.	λ(I. A)	Wave-no.	C-O
2	0	A_1		(Masked by 0,1α)	[21719]			Masked	[21789]	
		B_1	1^-(v)	4576.5	21845	1	$*0^+$	4561.5	21916	−1
3	1	A_1		Masked	[21702]			Masked	[21768]	
		B_1	1(v)	4580.8	21824	4	$*1^-$	4566.1	21894	0
4	2	A_1		Masked	[21684]			Masked	[21748]	
		B_1	—	.....	[21811]	—	$*0^-$	4570.7	21872	3
5	3	A_1		Masked	[21669]			Masked	[21732]	
		B_1	0	4586.9	21795	0	$*0^-$	4574.1	21856	2
1	0	A_1				−2				−2
		B_1				−3				−3
2	1	A_1								
		B_1	*4	4881.2	20481 (A_1)	1	$*1^+$	4872.8	20516	−2
3	2	A_1	5(v)	4850.9	20609 (B_1)	−1	2(v)	4842.9	20643	−3
		B_1				3				0
						1				0
0	0	A_1	1	5201.2	19221	−2				−3
		B_1	0(v)	5167.3	19347	−1				−2
1	1	A_1	$*1^-$	5195.5	19242	1		Heads		−2
		B_1	*00	5161.1	19370	−1		superposed		−4
2	2	A_1	1	5189.3	19265	0		on $B^{11}O$		−3
		B_1	1(v)	5155.5	19391	0		heads		−2
3	3	A_1	0?	5184.7	19282	7				8
		B_1	—		[19416]	—				—
4	4	A_1	0?	5176.1	19314	0				3
		B_1	—		[19441]	—				—
5	5	A_1	00?	5170.3	19336	5	On 0,0	B_1,$B^{11}O$	[19347]	—
		B_1	0?	5135.5	19467	1	1?(v)	5133.6	19474	0
0	1	A_1	—	Masked	[17981]	—	—	Masked	[17944]	
		B_1	—	by 0,3α	[18108]	—	—	by 0,3α	[18070]	
1	2	A_1	—		[18025]	—	—	Masked	[17988]	
		B_1	On 0,3 A_1 head		[18154]			by 0,3α	[18115]	
2	3	A_1	—	Masked	[18070]		—		[18036]	
		B_1	1^-	5493.7	18197	0	0(v)	5503.5	18165	−3
3	4	A_1	—	Masked	[18114]	—	—	Masked	[18085]	
		B_1	*0	5481.1	18240	2	0	5489.4	18212	−1
0	2	A_1			[16765]				[16692]	
		B_1	$*1^+$	5916.2	16898	−7	00?	5943.5	16821	−2
1	3	A_1	00?	5939.7	16831	−1	—		[16761]	—
		B_1	1^-(v)	5895.3	16958	−1	—		[16887]	—
2	4	A_1	—	On 0,2 B_1	[16895]	(−3)	—		[16831]	—
		B_1	0^+	5872.2	17025	−3	—	On 1,3 B_1	[16957]	—
3	5	A_1	—	On 1,3 B_1	[16961]	—	—	$B^{11}O$	[16903]	—
		B_1	—		[17088]	—	—		[17030]	—

Notes. The use of brackets, ? and *, and the dropping of half quantum numbers, are as explained under Table I, except that in the case of the (1,1), the (3,4)B, and the (0,2)B heads, the use of the * indicates superposition or merging with weak α system *heads* (cf. Table II) instead of structure lines. A (v) after an intensity value is here used to indicate distinct shading toward the violet. The calculated wave-numbers for the C-O column were obtained by adding 3 units to the values calculated from Eq. (10). Unidentified lines or heads occur at 16,785 (int. 00); 16,809 (00); 16864(00),—*P* head of 0,2 B_1?; 16928(0+),—*P* head of 1,3 B_1?; 19303(00); 19325(00); 19359(00); 19428(00+).

and n''. In the sequence for which $\Delta n=0$ (and presumably in those in which it is positive), the heads proceed toward the violet; in the sequence for which $\Delta n=-1$, the members of the sequence are all superposed to give what appears to be a single strong head: in the sequence $\Delta n=-2$, the heads proceed toward the red. In the $\Delta n=0$ sequence the $B^{10}O$ and $B^{11}O$ bands coincide; in the -1 sequence, the superposed members for $B^{10}O$ form an apparent single head which is correctly related, in respect both to position and intensity, to the corresponding $B^{11}O$ head; and so on. The above statements hold, furthermore, for both A_1 and B_1 heads, between which the $\Delta\nu$ separation is the same as that observed in the α system. The existence of these combination bands therefore affords striking confirmation of the general correctness of the preceding analysis of the α and β systems, and of their possession of a common final state.[39]

THE EXCITED STATES OF THE BO MOLECULE

Energy levels in BO. The electronic energy levels, with their associated vibrational levels, which are revealed by the foregoing analysis of the BO spectrum, and which may be deduced from Eqs. (8) and (9), are indicated in Fig. 1 by horizontal lines arranged on a vertical energy scale.[40] A set of more closely spaced rotational levels ($E^m=Bm^2+\ldots$.) should be imagined as superimposed above each vibrational level (and extending up across two or three higher vibrational levels).

The levels for both isotopes are shown on the same scale, thus illustrating the actual magnitude of the difference between them. The frequency corresponding to any band-origin is proportional to the distance from one of the upper (α or β) levels to one of the lower (N) levels. The vertical beaded lines indicate observed transitions for $B^{11}O$, the figure in each circle being the estimated photographic intensity of the head of the corresponding band. The difference in frequency for the two isotopes (isotopic displacement) for a given band, in relation to the position of the band with respect to the system-origin, depends on differences in energy of corresponding levels of the two isotopes in a way that can readily be seen from the diagram.

Constants of the BO molecule. The spacing of successive vibrational levels gives a measure of the corresponding molecular vibration frequency

[39] No new evidence is afforded as to the existence of half-vibrational quantum numbers. The calculated frequencies would not be appreciably changed if Eqs. (8) (9), and (10), like (1) and (2), had been formulated in terms of integral quantum numbers; this is because of the near-equality of the coefficients of n' and n''.

[40] Such diagrams were first used by R. T. Birge (Abstract, Phys. Rev. **23**, 294, 1924).

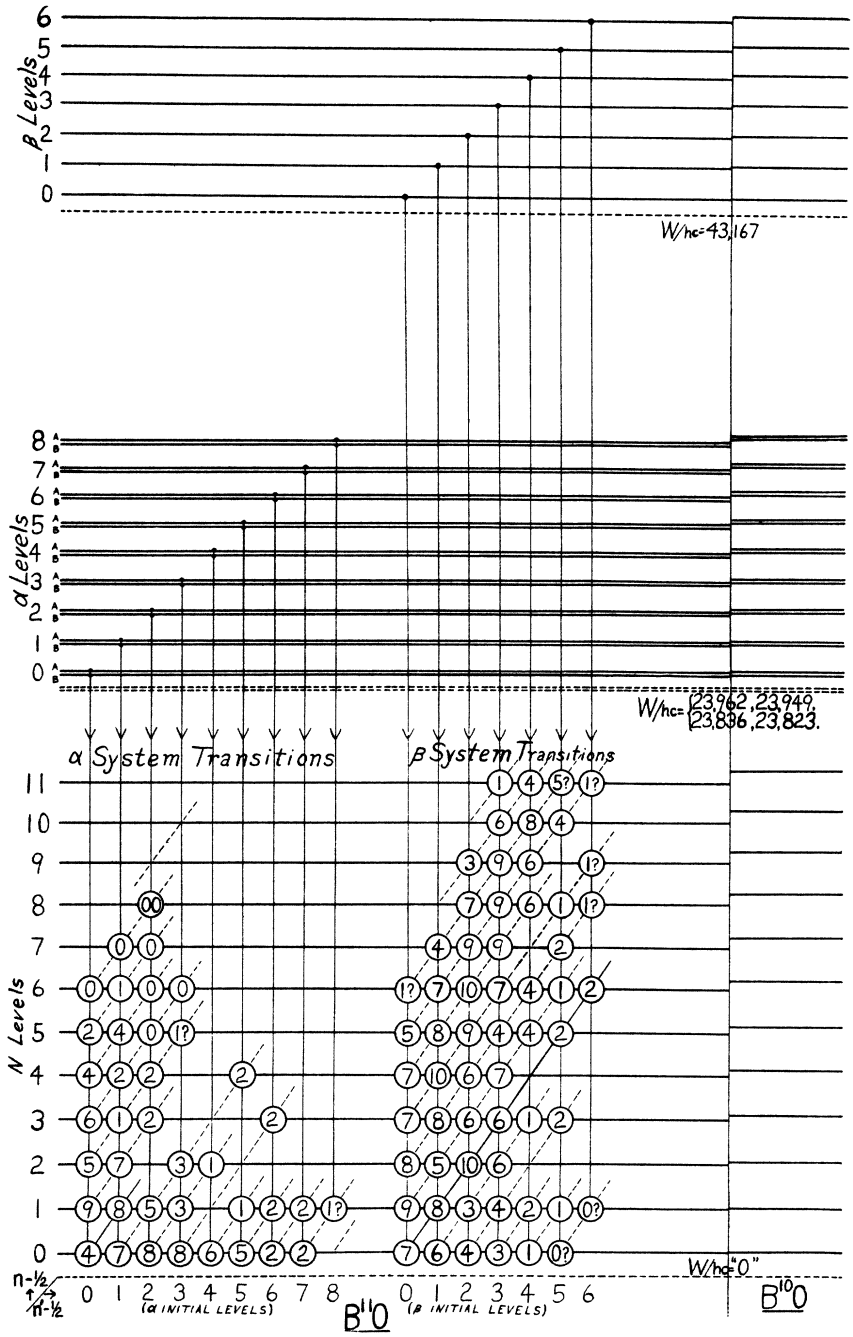

Fig. 1. *Vibrational energy levels and transitions in BO.*

DESCRIPTION OF FIG. 1

The α and β bands of BO involve two electronically excited sets of initial levels designated β and α, and a common final level designated N to indicate that it probably corresponds to the normal state of the molecule. The three electronic levels are shown for the vibrationless molecule ($n=0$), which probably does not exist, by dotted lines in Fig. 1; the lowest (N) is arbitrarily marked $E=0$. (In the figure, W was inadvertently used in place of E, also n in place of n''.) The vibrational levels, beginning with $n=\frac{1}{2}$, $1\frac{1}{2}$, . . . , which are associated with each electronic level, are drawn to scale in Fig. 1, the energy values being calculated from Eqs. (8) and (9). The $B^{10}O$ levels are shown on the extreme right, those of $B^{11}O$ occupying most of the figure. The α levels, shown *double* in Fig. 1, are really quadruple, each level of Fig. 1 being actually a close double.

A vertical line is drawn from each of the α levels toward the N levels; each intersection which is marked by a circle represents an observed $B^{11}O$ band, whose (estimated photographic) intensity is given by a number. For convenience in examining the intensity pattern, the initial vibrational quantum number (minus $\frac{1}{2}$) for each vertical row of circles is repeated at the bottom of the diagram. The diagonal lines between the circles serve to indicate *band-sequences*, i.e., sets of bands characterized by a particular value of $(n''-n')$.—Similar statements hold for the β system of bands. Note the very different character of the intensity distribution in the α and β systems. —The $B^{10}O$ transitions, which are not separately shown, are similar to those of $B^{11}O$.—In addition to the two systems of transitions shown, there is a third, of low intensity, corresponding to transitions from the β to the two α levels of Fig. 1.

ω. Quantitatively, according to the Bohr theory, $\omega=(1/h)\ (dE^n/dn)$. Then from Eqs. (8) and (9), for $B^{11}O$:

$$\omega_\beta=(1280.3-20.1n)\ c;\ \omega_\alpha=(1259.1-21.2n)\ c;$$
$$\omega_N=(1885.5-23.5n)\ c. \qquad (11$$

The subscripts of ω refer to the initial states of the β and α systems, respectively, and to their common final state; c is the velocity of light.

From the value of B_0 in Eqs. (5) and (7), since $B_0=h/8\pi^2\mu r_0^2$, the equilibrium internuclear distances r_0 for the three states can be calculated. These should of course be the same for both isotopes. The results are, in 10^{-8} cm, with a probable error of ± 0.03 in each case,[41]

$$r_\beta=1.16;\ r_\alpha=1.20;\ r_N=1.09. \qquad (12)$$

Note that the value of r_0 is very near that for CN, where $r_n=1.17$.

Possible analogy of BO and CN molecules to Na atom. There is considerable evidence for the existence of an analogy between CN and BO, both chemically unsaturated "odd molecules," and the Na atom. In all three cases, there are nine electrons outside the nuclei and K electrons. The CN molecule, like BO, emits two band systems having a common final state, which is in all probability the normal state of the molecule, as probably also in BO.[42] The α and β systems of BO then correspond to electronic resonance potentials 2.9 and 5.3 volts, and the red and violet bands of CN to 1.8 and 3.2 v. These may be compared with 2.10 and 3.74 v for the Na resonance potentials corresponding to the first two lines ($1s-2p$ and $1s-3p$) of the principal series of Na. Note that the ratio of the second to the first is 1.8 in all three cases. The "forbidden" transition $2p-3p$ in Na is furthermore paralleled by the absence in either BO or CN of a conspicuous band system corresponding to an

[41] It is *possible* that these results are incorrect: cf. ref. 33 and related discussion preceding Eq. (5).

[42] The maximum energy of the emitters of the BO β bands is about 6 v greater than that of a BO molecule in the N state (without vibration). If the N state were not the normal state, transitions to lower states would be expected. Barring the possibility of a metastable N state, such transitions should be accompanied by band emission. No bands of unknown origin are, however, observed between λ2000 and λ8500. It is very improbable that there is a system of bands lying wholly beyond λ8500. If there were bands beginning below λ2000, this would require for the BO molecule in its β state an energy of probably 14 volts. It is improbable that the BO molecule, with its odd number of electrons (N_2 ionizes at 16.3 v, NO at 9.4 v, etc.), could possess so high an electronic energy below ionization. Such a high energy is also improbable when one considers the energy of active N_2 (probably 10 or 11 v [22]) and of excited NO (probably about 6 v) in relation to the formation of excited BO molecules.—In regard to CN, see R. S. Mulliken, Nature, Dec. 13, 1924.

analogous transition from the upper to the lower of the two excited electron levels of the molecule. The occurrence in Na in low intensity of forbidden lines of this type is, however, matched in BO by the appearance of the weak $\beta \rightarrow \alpha$ system of bands.

The above analogies suggest the possibility that the first eight outer electrons in BO and CN may be arranged around the two nuclei in 2_1 and 2_2 orbits somewhat as in the octet of Na, the ninth electron being bound relatively loosely, perhaps in a 3_1 orbit, as in Na. Such binuclear octets would be in line with the probable structure of molecules of the HCl type, and with Langmuir's suggestion as to the structure of N_2, CO, CN^- ion, and the like. Proceeding from N_2 through O_2, one would then expect a gradual transition toward the typical shared octet of F_2.

If the α and β bands of BO, and the red and violet bands of CN, are really analogous, in respect to the electron transition involved, to the first two members of the principal series of Na, one may calculate approximate values of s and p spectral terms for these molecules. On this basis, the ionization potentials (equal to the $1s$ terms) should be about 4.4 volts for CN and about 7.0 v for BO. Higher members of the principal series of BO, if present, should lie in the unexplored ultraviolet below λ2000. In the case of CN, the origins of higher members should lie between about λ2800 and λ3300. Although the presence of additional CN band systems in this region has not been demonstrated, the *absence* of bands *below* the calculated series limit at λ2800 may well be significant. The ionization potentials just calculated for BO and CN suggest the existence of a parallelism among molecules to the alternation of higher and lower ionization potentials which is observed, in the case of atoms, as the number of valence electrons changes from even to odd. Thus: ·CN, BO (9 outer electrons), 4.4, 7.0 v; CO,N_2 (10 outer electrons), 14-15 v; 16. 3v; NO (11 outer electrons), 9.4 v; O_2 (12 outer electrons), 16.1 v.[43]

Intensity Relations and Structural Differences in Arc and Active Nitrogen Spectra of BO

Rotational energy distribution. As in the case of the CN bands,[44] and as would be expected for thermal equilibrium, the BO bands when generated in active nitrogen show a much smaller range of m' values (m = rotational quantum number) and a much lower maximum value of m',

[43] In regard to alteration of atomic ionization potentials cf. F. A. Saunders, Science, Jan. 18, 1924. Ionization potentials of CO, N_2, NO and O_2 are from compilation by K. T. Compton and F. L. Mohler, Bulletin of National Research Council on Critical Potentials, (1924).

[44] R. T. Birge, Astrophys. J. **55**, 273 (1922). Cf. also E. C. Kemble, Phys. Rev. **8**, 689 (1916); T. Heurlinger, Dissertation (Lund), pp. 65-6.

than when produced in the arc. This is illustrated in the case of the $(\frac{1}{2}\rightarrow 1\frac{1}{2})$ band in Plate I(*e*). Plate I(*f*) shows the general appearance of the β bands in the arc. Jevons' reproductions show their appearance in active nitrogen, and also show part of the α bands in both sources. The heads (for which m' is small), especially of $B^{10}O$, are notably less conspicuous in the arc, due to their reduced intensity and their concealment by structure lines of high m' from preceding heads.

Vibrational energy distributon. A study of the intensity data of Tables I and II, displayed in Fig. 1, gives interesting information. Thus by adding the intensity figures for all bands having a given n', one can get a rough idea of the initial n' distribution for the emitting molecules. In the β system, the number of molecules for a given value of n' appears to rise slightly from $n'=\frac{1}{2}$ to $n'=$about $2\frac{1}{2}$ or $3\frac{1}{2}$, falling off sharply after that, with a maximum n' of $5\frac{1}{2}$ or $6\frac{1}{2}$. In the α system, $n'=\frac{1}{2}$ and $1\frac{1}{2}$ are about equally prominent, after which there is a gradual falling off of intensity to n' values as high as $8\frac{1}{2}$. These n' distributions are evidently non-thermal, since for thermal equilibrium there should be a steady falling off of intensity with increasing n', with $n'=\frac{1}{2}$ by far the most prominent. The *arc spectra* of BO appear to approximate thermal equilibrium in respect to n' distribution. With respect to initial vibrational energy, the effective temperature appears to be actually higher in active nitrogen, which is really only a little above room temperature, than for the arc, while the reverse is the case with respect to rotational energy. The difference is well exemplified in Plate I(*e*), where the $(3\frac{1}{2}\rightarrow 3\frac{1}{2})$ β band appears strongly in active nitrogen, but is weak or apparently absent in the arc.

High n' values, unaccompanied by high m' values, also occur in other band spectra excited by active nitrogen, in cases where a chemical reaction is involved (e.g., CN, SiN). The high n' values developed by active nitrogen may presumably be attributed to the fact that the excitation of the second molecule is accomplished during a molecular collision, which one might naturally expect to produce a considerable amount of atomic vibration. The apparent absence of any appreciable increase of m' by such collisions is perhaps also to be expected.

Lenz, following a procedure first outlined by Heurlinger, has recently applied the Bohr correspondence principle with marked success to the problem of the relative intensity of groups of bands corresponding to different values of $(n''-n')$.[45] Using a simplified model, he has shown that the intensity distributions observed in various types of electronic band spectra may be accounted for, at least qualitatively. The important

[45] T. Heurlinger, Zeits. f. Phys. **1**, 87 (1920); W. Lenz, Zeit. f. Phys. **25**, 299 (1924)

factors are the nuclear vibration frequency, the frequency of motion of the emitting electron, and the amplitude of the perturbation of the electronic frequency by the vibrational motion. In the α system of BO, the intensity distribution of Δn values is fairly symmetrical about $\Delta n = 0$: the sequences $\Delta n = \pm 1$ are somewhat more intense than $\Delta n = 0$; for higher Δn's the intensity gradually diminishes; the maximum observed values are $\Delta n = -7$ and $+6$ ($\Delta n = +7$ lies too far into the infra-red for observation). In the β system, the observed Δn values range from -5 to $+8$, with a preponderance of intensity in favor of the positive Δn's. The latter are all about equally intense from 0 to $+6$, after which a rapid fall in intensity occurs. The comparative weakness of the negative Δn sequences may be due in part to the scarcity of molecules having $n' > 3\frac{1}{2}$; also it is *in part* only apparent, due to decreasing plate sensitivity. Lenz's theory predicts an approach to equality for numerically equal Δn values of opposite sign.

There appear to be a number of peculiar restrictions in the BO bands for particular changes $n' \rightarrow n''$. Thus in the α system, the sequence $\Delta n = 0$ is represented only by $(\frac{1}{2}, \frac{1}{2})$ and $(1\frac{1}{2}, 1\frac{1}{2})$, while in the β system, all values of n' except $4\frac{1}{2}$ are represented. Also, in the α system, the $(1\frac{1}{2}, 3\frac{1}{2})$, $(3\frac{1}{2}, 4\frac{1}{2})$, $(4\frac{1}{2}, 1\frac{1}{2})$, and $(4\frac{1}{2}, 3\frac{1}{2})$ bands are unexpectedly absent or nearly so, while the $(5\frac{1}{2}, 4\frac{1}{2})$ band is unexpectedly present. In the β system, many of the bands for which $n' = 4\frac{1}{2}, 5\frac{1}{2}$, and $6\frac{1}{2}$ are missing; e.g., $(4\frac{1}{2}, 2\frac{1}{2})$, $(4\frac{1}{2}, 3\frac{1}{2})$, $(4\frac{1}{2}, 4\frac{1}{2})$, $(4\frac{1}{2}, 7\frac{1}{2})$. A characteristic tendency shown by both systems is for the preferred values of Δn (either positive or negative) to increase with increasing n'.

A phenomenon probably closely related to the occurrence of large Δn values in the emission of band spectra seems to be indicated by the non-thermal occurrence of large n' values in gas spectra excited electrically in vacuum tubes at low temperatures. Apparently the excitation of a molecular electron by impact of an external electron is normally accompanied by a considerable increase in n. Direct evidence that electronic impacts readily produce nuclear vibration is to be found in the work of Brandt[46] on the 7 volt resonance potential in nitrogen.

Arc doublets. A very striking difference between the BO bands in the arc and in active nitrogen gives further information on the subject of collisions with excited molecules. In the case of the easily examined strong β bands $(1\frac{1}{2} \rightarrow \frac{1}{2})$, $(\frac{1}{2} \rightarrow \frac{1}{2})$, $(\frac{1}{2} \rightarrow 1\frac{1}{2})$, $(\frac{1}{2} \rightarrow 2\frac{1}{2})$, and $(\frac{1}{2} \rightarrow 3\frac{1}{2})$, each

[46] E. Brandt (Zeit. f. Phys. **8**, 32, 1921) finds that this is composed of a series of small breaks, of which each is doubtless an electronic resonance potential plus one of a variety of vibrational changes (cf. Fig. 1) analogous to a series of absorption bands $(0 \rightarrow 0)$ $(0 \rightarrow 1)$, ... , —or $(\frac{1}{2} \rightarrow \frac{1}{2})$, etc.

single positive branch line of the active nitrogen photographs is joined on the arc photographs by a companion, of equal intensity, in the direction of lower frequencies, so as to form a *doublet*.[47] The doublets are not resolved near the head; the separation first becomes noticeable at the 34th; 34th, 22nd, 18th, and 16th line, respectively, from the head for the above bands;[48] from this the doublet separation would seem to be considerably dependent on the final vibrational quantum number. At large distances from the head, neighboring doublets overlap. In Plate I(*e*) enlargements of the $(\frac{1}{2}\rightarrow 1\frac{1}{2})$ band in the arc and active nitrogen have been juxtaposed, and show well the arc doublets for $B^{11}O$; some of the $B^{10}O$ doublets can also be identified. In examining the reproduction, one must of course remember that the weak lines of the $(\frac{1}{2}\rightarrow 1\frac{1}{2})$ band of $B^{10}O$ are interspersed among (and sometimes superposed on) the stronger $B^{11}O$ lines; they are comparatively inconspicuous in the arc, but give in places a false doublet appearance in the active nitrogen photograph. The appearance of the doublets is entirely similar in the other bands mentioned.

Kratzer has shown that doublet bands may be explained by the assumption that the emitting molecules may possess resultant electronic angular momentum, either positive or negative, in the direction of molecular rotation.[49] If this explanation is correct, it would appear that in the instant of formation or excitation in active nitrogen, *one* only of the two possible relative directions of rotation is imparted to the BO molecule; while *both* directions appear under the conditions, presumably approaching thermal equilibrium, in the arc. Further elucidation of these interesting doublets and of the problem of the isolated positive branch must, however, be left until further more accurate measurements have been made.

In conclusion, it is a pleasure to acknowledge indebtedness to Prof. F. A. Saunders for his initial encouragement and later valuable advice and help. Much is also due to the kindness of the director of the laboratory, Prof. T. Lyman, and to the suggestions and criticism of Prof. E. C. Kemble. The writer is also indebted to Prof. G. P. Baxter of the Department of Chemistry for the pure boron chloride used.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
Sept. 12, 1924 (revised Dec. 11, 1924)

[47] The new lines appearing in the arc are almost certainly *not* the missing negative branch lines.

[48] It should be recalled that the dispersion is *decreasing* in the direction from $(1\frac{1}{2}\rightarrow\frac{1}{2})$ toward $(\frac{1}{2}\rightarrow 3\frac{1}{2})$.

[49] A. Kratzer, Ann. der Phys. **71**, 72 (1923); see also Zeit. f. Phys. **23**, 298 (1924).

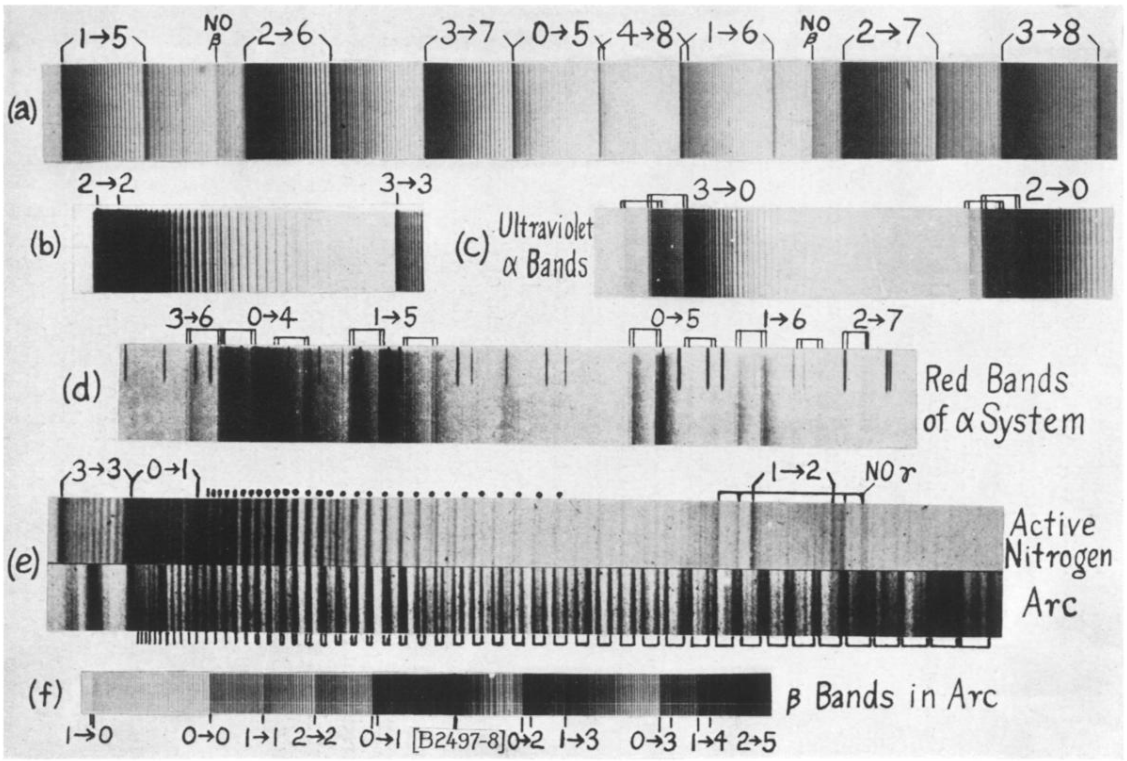

Plate I. *Enlargements of boron monoxide bands.*

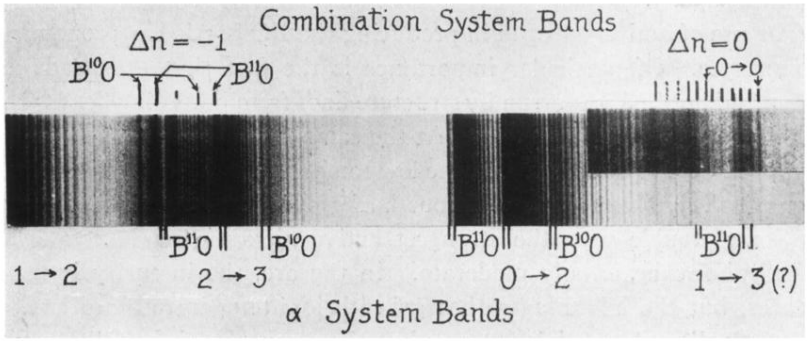

Plate II. Combination system bands, sequences $\Delta n = 0$ and $\Delta n = -1$.—The reproduction is enlarged from a single photograph, except for the insert in the upper right hand corner made from a longer exposure photograph, and showing better the $\Delta n = 0$ sequence. Note the faintness of the combination system bands as compared with the α system bands.—In both systems *A* heads are indicated with shorter, *B* heads with longer, lines adjacent to the reproduction.—Sequence $\Delta n = 0$. $B^{10}O$ and $B^{11}O$ heads superposed. Right to left—*A* heads 0→0, 1→1, 2→2, 3→3, 4→4, 5→5; then *B* heads 0→0, 1→1, 2→2, ... 5→5(?).—Sequence $\Delta n = -1$. Right to left,—superposed *A* heads, first of $B^{11}O$, then of $B^{10}O$; possible *P* branch head of *B* sequence of $B^{11}O$; superposed *B* heads, first of $B^{11}O$, then of $B^{10}O$.