Physics. — *Analysis of the β Bands of Boron Monoxide.* By A. ELLIOTT, B.Sc., Fellow of the Rockefeller Foundation. (Communication from the Physical Institute of the University of Utrecht). (Communicated by Prof. L. S. ORNSTEIN).

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Introduction.

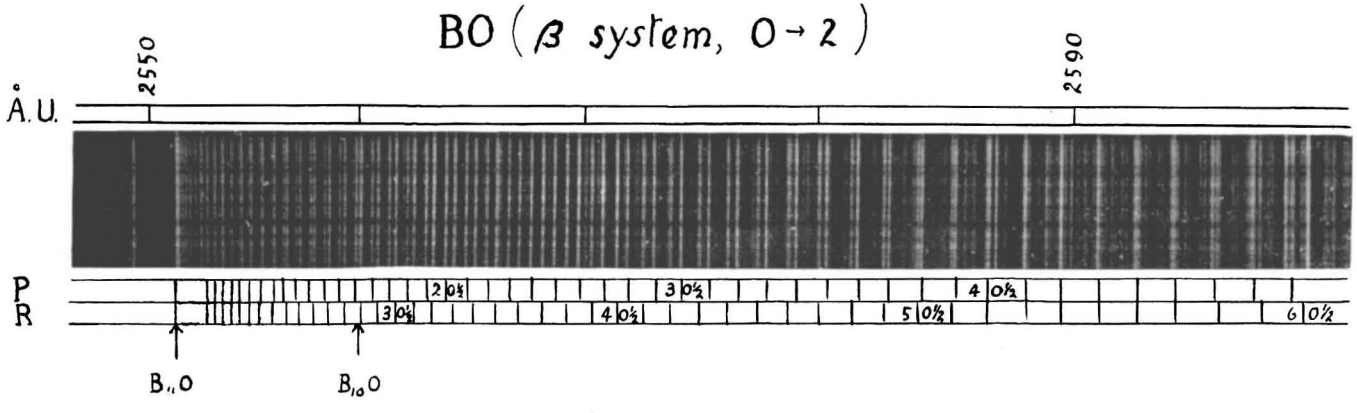
It is the purpose of this communication to describe a new interpretation of the structure of two of the β bands of boron monoxide. While the measurements to be described are adequate for the determination of the structure, further measurements are necessary before the rotation constants can be accurately determined, and the values given for the latter will probably need revision.

The bands of boron monoxide may be observed in an arc between carbons containing boric acid, and also in active nitrogen (containing a trace of oxygen), into which the vapour of boron trichloride is led. The latter source of the bands was discovered by Lord RAYLEIGH and the spectrum was measured and analysed by JEVONS (1), who attributed the spectrum to boron nitride on account of chemical evidence. The magnitude of the isotope effect points, however, as was shown by MULLIKEN (2), quite clearly to the monoxide of boron as the emitter of the spectrum.

Three electronic systems have been identified; the α system in the visible region ($^2\Pi \rightarrow {}^2\Sigma$), the β system in the ultra-violet ($^2\Sigma \rightarrow {}^2\Sigma$) and a weak intercombination system ($^2\Sigma \rightarrow {}^2\Pi$).

Some of the stronger α bands have been analysed by JENKINS (3), using the active nitrogen source, and more recently, SCHEIB (4) has analysed a number of the bands in the same system as they appear in the arc. Both investigators find the same structure; the different appearance of the spectra in the two sources is presumably in great measure due to the much higher temperature of the arc.

In the case of the β bands, however, important differences occur. MULLIKEN (loc. cit.) has pointed out that in these bands, in general, only one series of lines is to be observed in bands excited by active nitrogen, while two series of approximately equal intensity occur in the arc bands; one of the latter agrees in position with the single series of the former, and it was conjectured that this was an R branch. In a $^2\Sigma \rightarrow {}^2\Sigma$ transition, doublet P and R branches are to be expected, and MULLIKEN expressed the opinion that the second series of lines in the arc bands was not the missing P branch, but the other member of the


BO (β system, 0 → 2)
2550
2590
Å.U.
P
R
2 0½
3 0½
4 0½
5 0½
6 0½
3 0½
4 0½
B₁₁O
B₁₀O

R branch doublet, which was not excited in active nitrogen. In the absence of other evidence, this seemed probable, but as will appear, it is almost certainly not the case.

Experimental.

During the course of an investigation on the intensity ratios of the isotopic bands in boron monoxide, the author was led to examine the β bands in the arc. A HILGER $E1$ quartz spectrograph was used to photograph the region 2400—2600 Å.U., where the dispersion is about 3 Å.U. per mm.; a reproduction of one of the bands in this region, taken with an exposure of four minutes, is shown in the figure. A narrow slit was used, and since no appreciable temperature shift could occur in the short exposure time, the maximum resolution was obtained.

The doublets in the bands of $B_{11}O$ mentioned by MULLIKEN (loc. cit.) were examined, and it was found that, at some distance from the head, each member of a doublet was itself double, the separation being, however, greater for the series of lines which appears also in bands excited by active nitrogen. The (fine) doublet separation increases with distance from the band head, and resolution begins at about the thirty-sixth and forty-fifth lines from the head in the wider and narrower series of doublets, respectively.

The frequencies of the lines in the $0 \rightarrow 1$ and $0 \rightarrow 2$ bands were measured, using iron arc lines as standards. In these measurements, the lines from the twentieth to the fiftieth from the head have been measured, and since the determination of the fine doublet separation was not the immediate object of the work, the mean frequency of these doublets has been determined. More complete measurements will be carried out later, and the results will be published in greater detail.

Analysis.

The appearance of the arc β bands described above is just what would be expected for a $^2\Sigma \rightarrow {}^2\Sigma$ transition with all the branches present. Bands of this type have a P and an R branch, each of them consisting of doublets whose separation increases linearly with the rotation quantum number; a consequence of the connection between these latter is that, when the R branch forms the head and the doublets become resolved after this branch has turned at the head, the R lines are resolved nearer the origin than the P lines. Since the two bands measured have a common initial level, identical combination differences of the type $R(j) - P(j) = \triangle_2 F'$, where j is the effective quantum number in the lowest electronic level, should be found if the two series of fine doublets are P and R branches (neglecting the fine doubling).

Two such sets of combination differences have in fact been found and are given in columns (2) and (3) of the table. The agreement is good enough the make it exceedingly probable that they are genuine

Combination Differences.

	Upper State $\Delta_2 F'$		Lower State $\Delta_2 F''$	
	β bands		$0 \rightarrow 2$	
	$0 \rightarrow 1$	$0 \rightarrow 2$	β bands	α bands
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$27^1/_2$			190.1	190.39
$28^1/_2$			196.7	197.26
$29^1/_2$	176.4	175.9	203.5	204.06
$30^1/_2$	182.0	181.5	210.8	210.65
$31^1/_2$	187.8	187.4	217.3	217.73
$32^1/_2$	193.8	193.0	224 1	224.58
$33^1/_2$	199.4	199.0	231.0	231.18
$34^1/_2$	205.2	204.9	237.7	237.73
$35^1/_2$	210.7	210.6	244.6	244.74
$36^1/_2$	216.9	216.6	251.6	251.50
$37^1/_2$	222.5	222.4	258.1	258.30
$38^1/_2$	228.1	227.8	264.9	265.11
$39^1/_2$	233.8	233.9	271.8	272.02
$40^1/_2$	239.6	239.7	278.5	279.37
$41^1/_2$	245.1	244.9	285.5	285.85
$42^1/_2$	251.5	250.3	291.9	292.38
$43^1/_2$	256.7	256.4		

$B' = 1.53$ cm^{-1}.

$\Delta_2 F'$ values. A further test can, however, be applied, since the α and β systems have a common final level, and the $\Delta_2 F''$ values must therefore be identical for bands which have the same vibrational quantum number in the final state in the two systems. For the β bands, the values of $\Delta_2 F'' = R(j-1) - P(j+1)$ can readily be calculated from the line frequencies after the $\Delta_2 F'$'s have been determined.

For the α bands, SCHEIB (loc. cit.) gives the same combination differences for the $0 \rightarrow 2$ and $0 \rightarrow 3$ bands from his analysis; in columns (4) and (5) of the table these differences for the $0 \rightarrow 2$ band in both systems are reproduced. The agreement is such that there can be no doubt that the $\Delta_2 F''$'s for the β band are genuine. We may therefore conclude without hesitation that the two series of fine doublets are P and R branches, and that the bands have the structure of $^2\Sigma \rightarrow {}^2\Sigma$ bands.

Rotation Constants.

Since the α and β systems have the same final level, the values of B'' are the same for both. The measurements of SCHEIB (loc. cit.) are more complete than those of the writer, and his values of B'' more accurate than any which could be calculated from the present results. Consequently, only the value of B' has been calculated.

SCHEIB gives as the connection between the effective quantum number and series number m in his tables

$$m^+ + {}^1/_2 = m \text{ (here } m^+ \text{ is the writer's } j)$$

but there seems to be a mistake in the sign in this formula, for on extrapolating his lower state term differences one finds

$$m^+ - {}^1/_2 = m$$

and the numbering derived from this result leads to the same B'' values as he gives; apparently therefore the correct quantum numbers have been used in calculating the constants. The constant B' has been calculated from the equation

$$\triangle_2 F'/j = 4B'.$$

This equation is only approximate, since $\triangle_2 F'$ is not exactly linear in j, and the value found in this way for B' varies over the range of $\triangle_2 F'$ values available from 1.492 at $j = 29^1/_2$ to 1.474 at $j = 43^1/_2$. The variation is approximately linear, and the best value for B' has been found by extrapolating to $j = 0$, since at this point the above equation holds. This value is given under the table.

Comparison of the bands in the arc and in active nitrogen.

From a comparison of the $0 \rightarrow 1$ band in the arc and in active nitrogen, it has been found that in the latter it is the P branch which is missing, as was suspected by MULLIKEN (loc. cit.). The latter found that in two bands excited in active nitrogen ($2 \rightarrow 0$ and $4 \rightarrow 1$) a weak second series of lines was present; this was presumably the missing P branch. Traces were also found in other bands, but in general only one branch was to be observed. It may be remarked here that the lines of this branch may be double as in the arc, but since the rotation structure in the active nitrogen source is not strongly developed, it is not to be expected that the doublets will be resolved with the spectrographs hitherto employed.

The fact that the transition $j - 1 \rightarrow j$, corresponding to the missing P branch, occurs in the arc and not in excitation with active nitrogen is very remarkable. It is possible that the strong fields present in the arc may be connected with the phenomenon. An investigation of the intensities of P and R branches under different conditions in the arc may perhaps throw some light on the problem.

In conclusion, the author wishes to express his thanks to Prof. ORNSTEIN for the facilities and help given him during the course of the work.

Summary.

The $0 \rightarrow 1$ and $0 \rightarrow 2$ bands of the β system of BO are analysed and doublet P and R branches are found. The combination differences for the excited state in these two bands agree with each other. It is also found that the normal combination differences for the $0 \rightarrow 2$ band agree with those given by SCHEIB (4) for the $0 \rightarrow 2$ band in the α system in BO.

A comparison of the β bands excited in the arc and in active nitrogen shows that, as was suggested by MULLIKEN (2), it is the R branch which is present in the latter case; the P branch is usually absent.

REFERENCES.

1. W. JEVONS, Proc. Roy. Soc., **91A**, 120, 1914.
2. R. S. MULLIKEN, Phys. Rev. **25**, 259, 1925.
3. F. A. JENKINS, Proc. Nat. Acad. Sci., **13**, 496, 1927.
4. W. SCHEIB, Zeits. f. Physik, **60**, 74, 1930.