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Rotational Structure of the $^3\Sigma \rightarrow {}^3\Pi$ Bands of BF

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The rotational analysis has been made of the (0,0), (0,1), (0,2) and (1,0) bands of the *A* system of BF. The bands are interpreted in terms of a $^3\Sigma \rightarrow {}^3\Pi$ transition with coupling intermediate between case *a* and case *b*. The triplet separation of the upper ($^3\Sigma$) state is too small to be observed; that of the lower ($^3\Pi$) state is $-12.7B''$. The Λ-type splitting of the $^3\Pi$ states is less than 0.2 cm^{-1}. Other constants evaluated are: $B'_0=1.6235$, $B'_1=1.6030$, $D'_0=-4.2\times10^{-6}$, $D'_1=-9.7\times10^{-6}$, $B''_0=1.4030$, $B''_1=1.3851$, $B''_2=1.3672$, all in cm^{-1} units; $I'_e=16.93\times10^{-40}$ g cm^2, $I''_e=19.56\times10^{-40}$ g cm^2, and $r''_e=1.312\times10^{-8}$ cm.

THE band spectrum of BF is of interest because of its predicted similarity to the well-known spectra of CO and N_2. An earlier paper[1] from this laboratory reported on the spectrum of BF excited by means of an electrodeless discharge maintained in BF_3 gas. Sixteen of the bands obtained were assigned to two systems with a common lower electronic level. The present paper presents the rotational analysis of four bands of the *A* system, based on plates made in the same manner as the earlier ones, but with improved experimental conditions.

EXPERIMENTAL

The BF_3 gas used was obtained in a Pyrex flask from Booth and Willson of the Western Reserve University at the time of the earlier experiments. We transferred it to a carefully evacuated and baked out discharge tube by distillation at liquid-air temperatures. The discharge tube was provided with a quartz window, attached by means of a quartz to Pyrex graded seal. It was sealed off from the vacuum system while the BF_3 gas was solidified in a side arm by means of liquid air. The refrigeration of the side arm was then controlled to bring the pressure to a value suitable for producing an electrodeless discharge.

The oscillator used for exciting the discharge consisted of two 75-watt tubes, type 852, working in push-pull at a frequency of 20 megacycles. Plate current was obtained from a 2000-volt d.c. motor-driven generator. The power input was maintained at about 250 watts. The improved results obtained in the present experiments must be ascribed mainly to the superiority of this oscillator to the one used before, as the other conditions were substantially unchanged. The visible spectrum was examined frequently during the run, and it was found that the highest pressure at which the discharge could be maintained was most satisfactory for getting the BF bands. At low pressures, when the side arm became too cold, the Balmer lines of hydrogen showed up as an impurity.

An exposure of 30 hours was made with the 30,000-line, 21-foot grating of this laboratory. During the first 20 hours, the plates were half covered by metal shields supported independently of the plate-holder to provide both a 10-hour and a 30-hour exposure on each plate. An iron arc spectrum for wave-length comparisons was superimposed on part of the long exposure.

The dispersion in the first order is about 1.2A/mm at 3000A. A Geneva Society measuring engine was used in measuring the plates. The experimental error may be estimated as about 0.05 cm^{-1}. Measurements were made in both first and second order. The (0,0) band was measured in the third order also, but the resolution was no better than that obtained in the second order.

RESULTS

The appearance of the bands of this system is illustrated by Fig. 1, a reproduction of the (0,0) band, in which the assignments of the lines to branches are indicated. An anticipated similarity with bands of the CO molecule which was supported by the appearance of the bands suggested

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[1] H. M. Strong and H. P. Knauss, Phys. Rev. **49**, 740 (1936).

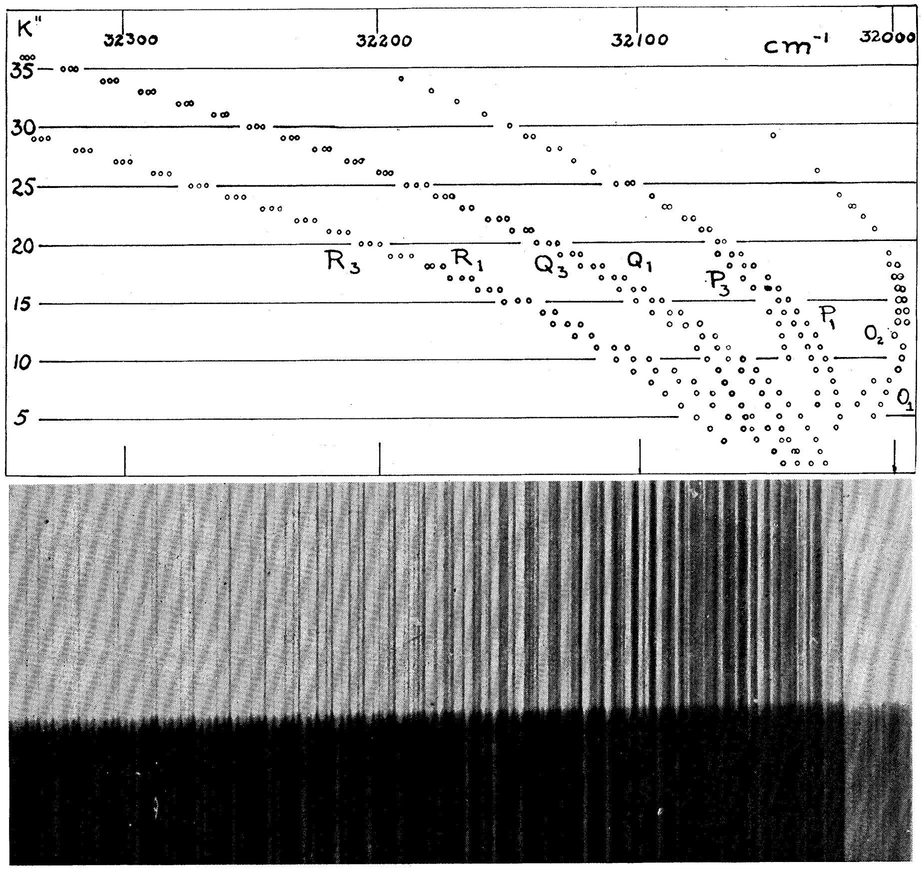

FIG. 1. Fortrat diagram and an enlargement of a part of the (0,0) band of the $^3\Sigma\rightarrow{}^3\Pi$ system of BF. The points are the identified members of the branches and are placed directly above the line so identified.

that the *A* system bands were, like the third positive system of CO, produced by a $^3\Sigma\rightarrow{}^3\Pi$ transition. Our analysis shows that this interpretation is correct.

A diagram showing the 27 branches of a $^3\Pi\rightarrow{}^3\Sigma$ transition allowed by the selection rules is given by Jevons.[2] In the third positive $^3\Sigma\rightarrow{}^3\Pi$ bands of CO, Dieke and Mauchly[3] found that the triplet separation of the $^3\Sigma$ state is so small that it can be neglected, thereby reducing the number of expected branches to 15, all of which they observed. The bands considered here have the same kind of structure, but show none of the strong perturbations which are present in CO. With the intensities present on our plates, we observed 11 branches of the possible 15. A schematic term diagram, Fig. 2, shows the observed transitions and indicates how the various branches are designated. The upper levels are drawn as triplets, although the triplet separation actually is too small to appear in our data. The subscripts 1, 2 and 3, are assigned in the order of increasing frequency. Lines are designated by means of K'' rather than J''.

In Table I are listed the band lines observed with visual estimates of the intensities, and assignments. Unassigned lines, present because of isotopic or other overlapping bands, have been omitted to save space. The assignments of J values were made graphically. In the tails of the bands, lines could be grouped into branches by inspection, and tentative assignments of J

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[2] W. Jevons, *Report on Band Spectra of Diatomic Molecules* (London, 1932), Fig. 45, p. 186.

[3] G. H. Dieke and J. W. Mauchly, Phys. Rev. **43**, 12 (1933).

values were made. These were adjusted to be consistent in the four bands studied. Rotational spacings in the upper ($^3\Sigma$) levels obtained from the various bands were found by listing $R_i(K)-Q_i(K)$ and $Q_i(K+1)-P_i(K+1)$, and similarly wave number differences characteristic of the lower ($^3\Pi$) levels were obtained as $R_i(K)-Q_i(K+1)$. The agreement of these values obtained from the different bands is typically within 0.1 cm^{-1}, which supports the validity of the assignments. No allowance has been made for the Λ-type doubling of the $^3\Pi$ levels, as we have been unable to evaluate it from our data, except to estimate an upper limit of 0.2 cm^{-1} for the Λ separation. If the Λ-type splitting were absent, $R_i(K)-Q_i(K)$ should equal $Q_i(K+1)-P_i(K+1)$. These two quantities show no consistent difference in our data.

The differences $R_i(K)-Q_i(K)$ for the different bands show rather large variations from each other in the region of low values of K. These variations are attributed to inaccuracy in the evaluation of the wave numbers of the lines, due to lack of resolution.

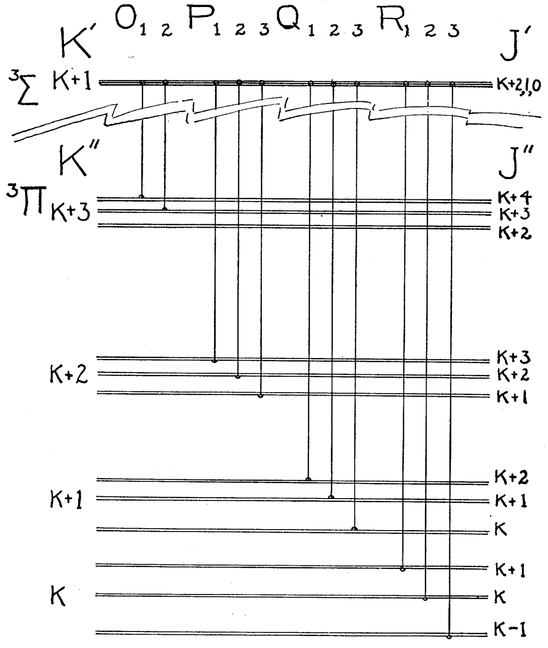

FIG. 2. Schematic diagram of the observed transitions between $^3\Sigma$ upper states and $^3\Pi$ lower states in BF. The designations of the various branches are shown at the top of the diagram. The multiplet splitting of the upper state and the Λ-type splitting of the lower state are indicated although they are too small in magnitude to be evaluated.

In order to evaluate the molecular constants B and D it is necessary to apply the theory of Gilbert[4] for the case of coupling intermediate between case a and case b. This has been done approximately, by ignoring Λ-type doubling, and neglecting possible terms in $J^3(J+1)^3$. The Q and R branches have been used to determine the constants of the $^3\Pi$ state, since the P branches are not well developed in this system of bands. If we write

$$\Delta_2 W_i(J)=R_i(J)-Q_i(J+1)+R_i(J-1)-Q_i(J),$$

the sum of these quantities can be used as an approximation to $\Sigma\Delta_2 W_i(J)$ in Gilbert's equation. The molecular constants obtained by this method are given in Table II.

The value of $\lambda = A/B$ for the bands has been obtained graphically from the experimental data by the method described by Challacombe and Almy.[5] The best value for this constant was found to be $\lambda=-12.7$. With this value and the values of B'' previously obtained, the constant A was found to be -17.81 for (0,0); -17.59 for (0,1), and -17.36 for (0,2). This gives the multiplet splitting in cm^{-1} for the $^3\Pi$ states. The minus sign indicates that the multiplet structure is inverted. This result is corroborated by the rotational analysis, as it is found that the rotational levels designated as F_3 go over into the $^3\Pi_0$ levels at low K values, and the F_1 levels go over into the $^3\Pi_2$ levels.

The data for the (0,0), (0,1) and (1,0) bands permitted an unambiguous extrapolation to determine B_v''. The slopes of the straight lines used for these bands were all negative and of the order of 10^{-6} cm^{-1}. They do not seem to us to be significant because an approximation was used in determining $\Delta_2 W_i(J)$. In the case of the (0,2) band, a plot of $\Sigma\Delta_2 W_i(J)/6(2J+1)$ against $J(J+1)$ gives a curved instead of a straight line, which indicates either that the Λ-type doubling has a larger effect in this band than in the others, or that a term in $J^3(J+1)^3$ is present in the rotational energy. Extrapolation of the curve which best fits the experimental points gives $B_2''=1.3472$. Extrapolation of a straight

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[4] Cecil Gilbert, Phys. Rev. **49**, 619 (1936).

[5] C. N. Challacombe and G. M. Almy, Phys. Rev. **51**, 930 (1937).

TABLE I. *Rotational structure of (0,0), (0,1), (0,2) and (1,0) bands of* BF. *D* = *diffuse and db* = *double.*

INT. (EST.)	ν OBS. CM⁻¹	ASSIGNMENT
	(0,0)	Band
5	31994.96	$O_1$13, 14
1	95.87	$O_1$11, 15
2	96.98	$O_1$10, 16
2	97.46	$O_1$17
2	98.40	$O_1$9; $O_2$14, 15
3	99.06	$O_1$18; $O_2$13, 16
3*db*	32000.05	$O_2$12, 17
3*db*	01.25	$O_1$8, 19: $O_2$8
4	02.46	$O_1$7
2	04.16	$O_1$20
3	04.81	$O_1$6
2	06.72	$O_1$21
3	07.65	$O_1$5; $O_2$8
4	10.54	$O_1$22; $O_2$7
3	13.63	$O_2$6
0	14.84	$O_1$23
2	16.27	$O_2$23
10	20.49	$O_2$24; $P_1$5
3	21.15	$P_1$6
4	21.90	$O_2$4; $P_1$7
5	23.07	$P_1$8
6	24.44	$P_1$9
10	26.23	$P_1$10; $Q_1$1
3	28.32	$Q_1$2; $P_1$11
20*db*	29.34	$O_1$26; $P_2$6, 7
10	30.76	$Q_1$3; $P_1$12; $P_2$9
3	32.05	$R_1$1; $P_2$10
20*db*	33.67	$Q_1$4; $P_1$13; $P_2$11
4	35.92	$Q_1$5; $P_2$12
5	37.01	$R_1$2; $P_1$14; $Q_2$1
20*db*	38.65	$Q_2$2; $P_2$13
5	40.67	$P_3$10; $Q_1$6; $P_1$15; $Q_2$3
1	41.62	$P_3$11; $P_2$14
2	42.29	$R_2$1
1	43.11	$P_3$12; $R_1$3; $Q_2$4
20	44.89	$P_3$13; $Q_1$7; $P_1$16; $Q_2$5; $P_2$15
3	47.12	$O_1$29; $R_2$2
1?	48.38	$P_3$14; $Q_2$6
15	49.20	$R_1$4; $Q_1$8; $P_1$17; $P_2$16
4	51.71	$Q_2$7
10	53.78	$Q_3$3; $Q_1$9; $R_2$3
8	54.29	$P_3$16; $P_1$18
5	55.38	$Q_3$4; $R_1$5; $Q_2$8
5	57.40	$Q_3$5; $P_2$18
10	58.66	$P_3$17; $Q_1$10; $R_2$4
8	59.65	$Q_3$6; $P_1$19; $Q_2$9
5	62.44	$Q_3$7; $P_2$19
2*db*?	63.38	$P_3$18; $R_1$6
5	64.15	$Q_1$11; $R_2$5; $Q_2$10
8	65.40	$Q_3$8; $P_1$20
2	66.29	$R_2$3
2	68.55	$Q_3$9; $P_3$19; $P_2$20
5	69.20	$Q_2$11
2	69.86	$Q_1$12
1	70.50	$R_1$7; $R_2$6
3*db*	77.49	$R_3$4; $P_1$21
5	72.46	$Q_3$10
5	74.59	$Q_2$12; $P_2$21
5	76.04	$Q_1$13
5	76.90	$R_3$5; $Q_3$11; $R_2$7
20*tr*	78.54	$R_1$8; $P_1$22
5	80.42	$Q_2$13; $P_2$22
8	81.74	$Q_3$12
8	82.45	$R_3$6; $Q_1$14
1	83.71	$R_2$8
4*db*	85.32	$R_1$9
8*D*	86.94	$Q_3$13; $P_1$23; $Q_2$14
2	87.77	$R_3$7; $P_2$23
5	89.55	$Q_1$15
2	92.30	$R_2$9
20*db*	93.22	$Q_3$14; $P_1$24; $Q_2$15
1	93.93	$R_3$8
2	94.52	$R_1$10
5	96.89	$Q_1$16
5	99.36	$Q_3$15
15*db*	32100.49	$R_3$9; $R_2$10; $Q_2$16
1	01.51	$P_1$25
2	03.15	$R_1$11; $P_2$25
4	04.67	$Q_1$17
3	06.20	$Q_3$16
1	07.62	$R_3$10; $P_3$25
5*tr*	08.24	$R_2$11; $Q_2$17
4	12.82	$Q_1$18
5	13.46	$Q_3$17
5	15.30	$R_3$11
5	16.21	$P_3$26; $Q_2$18
5	17.22	$R_2$12
20	32121.35	$Q_3$18; $R_1$13; $Q_1$19
3	23.51	$R_3$12
2	24.02	$P_3$27
4	24.68	$Q_2$19
2	26.27	$R_2$13
4	29.47	$Q_3$19; $P_2$28
5	30.49	$Q_1$20
1	31.15	$R_1$14
3	32.13	$R_3$13
8	33.55	$P_3$28; $Q_2$20
2	35.82	$R_2$14
5	38.17	$Q_3$20
1	39.21	$P_2$29
4	40.09	$Q_1$21
5	41.38	$R_1$15
5	42.90	$P_3$29; $Q_2$21
3	45.77	$R_2$15
5	47.36	$Q_3$21
1	48.51	$P_2$30
4	49.98	$Q_1$22
2	50.94	$R_3$15
1	51.96	$R_1$16
5	52.69	$Q_2$22
2	56.21	$R_2$16
5	56.95	$Q_3$22
3	58.23	$P_2$31
4	60.25	$Q_1$23
4	61.01	$R_3$16
5	63.00	$R_1$17; $Q_2$23
5	66.99	$Q_3$23; $R_2$17
2	68.46	$P_2$32
4	71.06	$Q_1$24
4	71.60	$R_3$17
3	73.58	$Q_2$24
3	74.44	$R_1$18
4	77.50	$Q_3$24
2	78.30	$R_2$18
1	79.09	$P_2$33
10	82.41	$R_3$18; $Q_1$25
5	84.66	$Q_2$25
3	86.33	$R_1$19
5	88.46	$Q_3$25
3	90.12	$R_2$19; $P_2$34
10	93.96	$R_3$19; $Q_1$26
3	96.21	$Q_2$26
3	98.52	$R_1$20
4	99.85	$Q_3$26
5	32202.13	$R_2$20
8	06.01	$R_3$20; $Q_1$27
5*D*	08.18	$Q_2$27
5	11.69	$Q_3$27; $R_1$21
3	14.74	$R_2$21
8	18.40	$R_3$21; $Q_1$28
4	20.51	$Q_2$28
8*D*	24.17	$Q_3$28; $R_1$22
2	27.75	$R_2$22
5	31.33	$R_3$22; $Q_1$29
4	33.51	$Q_2$29
4	36.75	$Q_3$29
2	37.90	$R_1$23
3	41.12	$R_2$23
10	44.64	$R_3$23; $Q_1$30
3	46.69	$Q_2$30
3	49.99	$Q_3$30
2	51.90	$R_1$24
3	55.07	$R_2$24
5	58.41	$R_3$24; $Q_1$31
2	60.44	$Q_2$31
2	63.59	$Q_3$31
2	66.28	$R_1$25
3	69.33	$R_2$25
8*db*	72.62	$R_3$25; $Q_1$32
2	74.65	$Q_2$32
4	77.68	$Q_3$32
2	81.04	$R_1$26
3	84.07	$R_2$26
3	87.39	$R_3$26; $Q_1$33
3	89.21	$Q_2$33
3	92.27	$Q_3$33
1	96.37	$R_1$27
2	99.22	$R_2$27
2	32302.54	$R_3$27; $Q_1$34
3*db*?	04.32	$Q_2$34
1	07.25	$Q_3$34
2	12.11	$R_1$28
2	15.00	$R_2$28
2	18.17	$R_3$28; $Q_1$35
4	19.93	$Q_2$35
2	22.72	$Q_3$35
5	28.24	$R_1$29
2	31.04	$R_2$29
2	32334.22	$R_3$29; $Q_1$36
2	35.82	$Q_2$36
3	38.70	$Q_3$36
	(0,1)	Band
4	30716.28	$P_1$5, 6
3	17.24	$P_1$7
5	18.63	$P_1$8
8	20.23	$P_1$9
2	22.81	$P_1$10
5*db*	24.89	$P_1$11; $P_2$6, 7
5*D*	26.39	$P_2$8, 9
20*D*	27.96	$P_1$12; $P_2$10
3	30.15	$P_2$11
3	30.98	$P_1$13
1	31.88	$Q_1$5
5	32.76	$P_2$12
15*db*?	34.38	$P_3$6, 7
10	35.83	$P_3$5, 8; $Q_1$6; $P_1$14; $P_2$13
0	37.95	$P_3$11
10	39.13	$P_3$4; $P_1$15; $P_2$14
4	40.28	$P_3$3, 12; $Q_1$7; $Q_2$5
10	43.56	$P_1$16; $Q_2$6
6	44.77	$R_1$4; $Q_1$8
3	45.41	$P_3$14
3	47.08	$Q_2$7; $P_2$16
8	48.71	$Q_3$2; $P_3$15; $P_1$17
5	49.80	$Q_3$3; $Q_1$9
2	51.08	$Q_3$4; $R_1$5; $Q_2$8
2	51.73	$Q_3$5; $P_2$17
2	53.39	$P_3$16
3	54.28	$Q_3$6; $P_1$18
8*db*	55.28	$Q_1$10; $Q_2$9
4	56.88	$Q_3$7; $P_2$18
10*D*, *db*	58.05	$R_3$2; $P_3$17; $R_1$6
15*db*	60.50	$Q_3$8; $Q_1$11; $P_1$19; $Q_2$10
2	62.27	$R_3$3
8*db*	64.08	$Q_3$9
3	65.70	$R_2$6; $Q_2$11
5	66.76	$R_3$4; $R_1$7; $Q_1$12; $P_1$20
4	68.51	$Q_3$10; $P_3$19
1	69.59	$P_2$20
5	71.48	$R_3$5; $Q_2$12
4	72.10	$R_2$7
10	73.37	$Q_3$11; $Q_1$13
5	73.85	$P_1$21
1	74.39	$P_3$20; $R_1$8
1	75.82	$P_2$21
8	77.09	$R_3$6
5	77.75	$Q_2$13
5	78.55	$Q_3$12
20*db*?	80.72	$P_3$21; $Q_1$14; $P_1$22
2	82.08	$R_3$7; $R_1$9
4	83.04	$P_2$22
15	84.42	$Q_3$13; $Q_2$14
8	87.75	$Q_1$15; $R_2$9
1	88.66	$P_3$22; $P_1$23
3	89.35	$R_3$8
5	90.69	$Q_3$14; $R_1$10; $P_2$23
5*db*	91.80	$Q_2$15
5	95.67	$P_3$23; $Q_1$16
5	96.35	$R_3$9; $R_2$10
5	97.47	$Q_3$15; $P_1$24
8	99.40	$R_1$11; $Q_2$16; $P_2$24
5	30803.90	$R_3$10; $P_3$24; $Q_1$17
5	04.89	$Q_3$16; $R_2$11
2	05.95	$P_1$25
4	07.43	$Q_2$17; $P_2$25
3	08.92	$R_1$12
4	11.82	$R_3$11
8	12.75	$Q_3$17; $Q_1$18
3	14.08	$P_1$26; $R_2$12
4	16.00	$Q_2$18
1	16.52	$P_2$26
2	18.80	$R_1$13
3	20.32	$R_3$12
5	20.96	$Q_3$18; $P_3$26
4	21.96	$Q_1$19
4	23.62	$R_2$13
6	25.05	$P_1$27; $Q_2$19
2?	29.18	$R_1$14
4	29.79	$R_3$13; $Q_3$19
1	30.53	$P_3$27
8	31.68	$Q_1$20
2	33.61	$R_2$14
8	34.74	$P_1$28; $Q_2$20
1	37.10	$P_2$28
5	39.07	$Q_3$20
3	30839.55	$R_3$14; $R_1$15
2	40.48	$P_3$28
4	41.77	$Q_1$21
2*db*?	43.92	$R_2$15
4	44.61	$Q_2$21
2	45.60	$P_1$29
2	46.95	$P_2$29
6	49.02	$R_3$15; $Q_3$21
3	50.83	$R_1$16
1	51.68	$P_3$29
4	52.37	$Q_1$22
6	55.01	$R_2$16; $Q_2$22
1	56.73	$P_1$30
10	59.42	$R_3$16; $Q_3$22
4	62.10	$P_3$30; $R_1$17
4	63.43	$Q_1$23
6	66.13	$R_2$17; $Q_2$23
0	68.33	$P_1$31
5	70.05	$Q_3$23
5	70.79	$R_3$17
1	73.35	$P_3$31
2	74.25	$R_1$18
4	74.98	$Q_1$24
4	77.44	$Q_2$24
2	78.09	$R_2$18
1	80.57	$P_1$32
4	81.32	$Q_3$24
2	82.36	$R_3$18
2	85.33	$P_3$32
8	86.88	$R_1$19; $Q_1$25
5	89.32	$Q_2$25
2	90.40	$R_2$19
5	93.04	$Q_3$25; $P_1$33
4	94.39	$R_3$19
2	97.77	$P_3$33
5	99.53	$R_1$20; $Q_1$26
3	30901.72	$Q_2$26
3	03.22	$R_2$20
4	05.32	$Q_3$26
3	06.97	$R_3$20
2	10.68	$P_3$34
4	12.35	$Q_1$27
4	13.01	$R_1$21
4	14.57	$Q_2$27
3	16.45	$R_2$21
5	18.06	$Q_3$27
5	19.99	$R_3$21
1	24.09	$P_3$35
4	25.77	$Q_1$28
2	26.84	$R_1$22
4	27.85	$Q_2$28
3	30.12	$R_2$22
4	31.27	$Q_3$28
4	33.55	$R_3$22
3	38.08	$P_3$36
4	39.66	$Q_1$29
3	41.10	$R_1$23
3	41.62	$Q_2$29
2	44.31	$R_2$23
3	44.92	$Q_3$29
4	47.62	$R_3$23
4	53.99	$Q_1$30
5	55.92	$R_1$24; $Q_2$30
5	59.05	$Q_3$30; $R_2$24
2	62.10	$R_3$24
1	67.05	$P_3$38
3	68.78	$Q_1$31
10*D*	70.85	$R_1$25; $Q_2$31
10	73.90	$Q_3$31; $R_2$25
2	77.10	$R_3$25
1	82.33	$P_3$39
4	84.03	$Q_1$32
3	85.90	$Q_2$32
3	86.70	$R_1$26
3	88.86	$Q_3$32
3	89.64	$R_2$26
4	92.59	$R_3$26
2	99.74	$Q_1$33
2	31001.55	$Q_2$33
2	02.86	$R_1$27
3	04.53	$Q_3$33
2	05.74	$R_2$27
2	08.48	$R_3$27
2	15.99	$Q_1$34
2	17.67	$Q_2$34
2	19.42	$R_1$28
3	20.53	$Q_3$34
2	22.22	$R_2$28
3	24.91	$R_3$28
3	32.76	$Q_1$35
3	34.30	$Q_2$35

TABLE I. (*Continued*).

INT. (EST.)	ν OBS. CM^{-1}	ASSIGNMENT
	(0,1)	Band
2	31036.55	$R_1$29
3*db*?	37.10	$Q_3$35
3	39.29	$R_2$29
4	41.84	$R_3$29
	(0,2)	Band
3*D*	29409.18	$O_1$10, 11, 12, 13
3*D*	10.57	$O_1$14, 9
1	11.63	$O_1$8, 15
3	13.12	$O_1$7, 16; $O_2$11, 12, 13
2	13.75	$O_2$14
1?	14.49	$O_2$10, 15
2	16.01	$O_1$6; $O_2$16
3	17.32	$O_2$9
5	17.65	$O_2$17
5*db*?	20.24	$O_1$5
2	23.82	$O_2$19
2	25.26	$O_1$20
3	29.70	$O_1$21
4*db*	31.56	$O_2$21; $P_1$6
3	32.55	$P_1$7
4*db*?	33.98	$P_1$8
5*db*?	36.14	$O_2$22; $P_1$9
2	38.40	$P_1$10
4*db*?	39.58	$P_2$5, 6
2	40.51	$P_2$7
3	41.16	$P_2$8; $P_1$11
2	42.01	$P_2$9
2	42.73	$P_2$10; $Q_1$31
5*db*	44.18	$P_1$12
1	45.28	$Q_1$4
4	46.49	$P_2$11
4	48.14	$P_1$13; $Q_1$5
5	49.29	$Q_2$2; $P_2$12
3	50.81	$P_3$7, 8; $Q_2$3
2	51.15	$P_3$9; $Q_1$6
4	52.29	$P_3$10; $P_2$13; $P_1$14
4	52.97	$Q_2$4
2	53.52	$P_3$11
6*db*	55.19	$Q_2$5; $R_1$3; $Q_1$7
3	56.78	$P_3$12; $P_2$14; $P_1$15
5	58.25	$R_2$2; $Q_2$5
3	59.97	$P_2$15; $Q_1$8
2	61.10	$R_1$4
5	61.92	$Q_2$7; $P_1$16
1?	62.96	$P_3$14; $R_2$3
2	65.18	$Q_3$3; $P_2$16; $Q_1$9
5	66.10	$Q_3$4; $Q_2$8
3	67.50	$Q_3$5; $P_1$17; $R_1$5
1	68.44	$R_2$4
2	69.59	$Q_3$6
5	70.72	$Q_2$9; $P_2$17; $Q_1$10
1?	71.37	$P_3$16
3	72.25	$Q_3$7
3	73.81	$R_2$5; $P_1$18; $R_1$6
6	75.74	$Q_3$8; $Q_2$10
2	76.71	$P_2$18; $Q_1$11
4	77.60	$R_3$3
3	79.53	$Q_3$9
2	80.10	$R_2$6; $P_1$19
1	81.04	$R_1$7
5	81.61	$R_3$4; $Q_2$11
3	83.22	$Q_1$12
5	83.93	$Q_3$10
2	86.22	$R_3$5
2	87.12	$R_2$7; $P_1$20
5*db*?	87.80	$P_3$19; $Q_2$12
3	89.08	$Q_3$11; $R_1$8
2	90.18	$Q_1$13
2	91.56	$R_3$6
10	94.56	$Q_3$12; $P_3$20; $R_2$8; $Q_2$13; $P_1$21
5	97.53	$R_3$7; $R_1$9; $Q_1$14
3	29500.91	$Q_3$13
5	01.58	$Q_2$14
2	02.75	$P_1$22
3	03.52	$R_2$9
3	04.10	$R_3$8
3	05.41	$Q_1$15
2	06.19	$R_1$10
3	07.67	$Q_3$14
4	09.26	$Q_2$15
3	11.37	$R_3$9; $R_2$10; $P_1$23
2	13.77	$Q_1$16
2	14.93	$Q_3$15
1	29515.46	$R_1$11
5*db*?	17.42	$Q_2$16
2	19.11	$R_3$10
2	20.38	$R_2$11; $P_1$24
8	22.71	$Q_3$16; $Q_1$17
1	25.28	$R_1$12
3	25.99	$Q_2$17
4	27.53	$R_3$11
5*db*	30.10	$R_2$12; $P_1$25
3	31.18	$Q_3$17
3	31.92	$Q_1$18
8*db*	35.20	$Q_2$18; $R_1$13
2	36.41	$R_3$12; $P_3$25
5	40.07	$Q_3$18; $R_2$13; $P_1$26
3	41.73	$Q_1$19
2	44.78	$Q_2$19
3	45.90	$R_3$13; $P_3$26; $R_1$14
4	49.50	$Q_3$19
4	50.55	$R_2$14
3	52.04	$Q_1$20
3	54.97	$Q_2$20
3	56.00	$R_3$14; $P_3$27
1	57.23	$R_1$15
3	59.48	$Q_3$20
2	61.62	$R_2$15
3	62.84	$Q_1$21
3	65.64	$Q_2$21
2	66.54	$R_3$15
1	66.98	$P_3$28
2	68.87	$R_1$16
4	69.94	$Q_3$21
4	73.06	$R_2$16
4	74.18	$Q_1$22
2	76.85	$Q_2$22
2	77.65	$R_3$16
1	78.53	$P_3$29
4	80.98	$Q_3$22; $R_1$17
3*D*	84.96	$R_2$17
4	85.95	$Q_1$23
4	88.54	$Q_2$23
3	89.27	$R_3$17
1	90.37	$P_3$30
4	92.50	$Q_3$23
2	93.52	$R_1$18
3	97.32	$R_2$18
4	98.26	$Q_1$24
4	29600.69	$Q_2$24
2	01.45	$R_3$18
1*db*	02.89	$P_3$31
4	04.55	$Q_3$24
2	06.56	$R_1$19
3	10.21	$R_2$19
4	11.08	$Q_1$25
4	13.44	$Q_2$25
3	14.17	$R_3$19
1	15.74	$P_3$32
4	17.12	$Q_3$25
2	20.13	$R_1$20
2	23.59	$R_2$20
3	24.43	$Q_1$26
3	26.58	$Q_2$26
2	27.36	$R_3$20
1	29.30	$P_3$33
3	30.17	$Q_3$26
2	34.17	$R_1$21
3	37.58	$R_2$21
3	38.17	$Q_1$27
4	40.35	$Q_2$27
4	41.10	$R_3$21
2	43.25	$P_3$34
4	43.81	$Q_3$27
2	48.68	$R_1$22
2	52.01	$R_2$22
3	52.43	$Q_1$28
2	54.54	$Q_2$28
3*db*	55.40	$R_3$22
3	57.86	$Q_3$28
3	63.71	$R_1$23
8*db*	67.06	$R_2$23; $Q_1$29
3	69.20	$Q_2$29
2	70.05	$R_3$23
5	72.47	$Q_3$29
1	79.14	$R_1$24
5	82.38	$R_2$24; $Q_1$30
3*db*	84.33	$Q_2$30
2	85.38	$R_3$24
2	87.56	$Q_3$30
2	29695.12	$R_1$25
4	98.15	$R_2$25; $Q_1$31
4	29700.05	$Q_2$31
2	01.03	$R_3$25
3	03.11	$Q_3$31
3	11.57	$R_1$26
4	14.47	$R_2$26; $Q_1$32
3*db*	16.34	$Q_2$32
2	17.31	$R_3$26
4	19.20	$Q_3$32
3	28.59	$R_1$27
5	31.30	$R_2$27; $Q_1$33
3	32.97	$Q_2$33
3	34.08	$R_3$27
4	35.92	$Q_3$33
5	48.73	$R_2$28; $Q_1$34
4	50.10	$Q_2$34
4	51.48	$R_3$28
5*db*	53.28	$Q_3$34
	(1,0)	Band
2	33576.72	$O_1$13
1	79.10	$O_1$18, 19; $O_2$15, 16
2	80.65	$O_1$11; $O_2$14, 17, 18
2*D*	82.64	$O_1$9; $O_2$12
2*db*	84.53	$O_1$8, 21
1	86.04	$O_1$22; $O_2$10, 21
2	87.02	$O_1$7
1	88.41	$O_2$22
2	89.63	$O_1$23; $O_2$9
1	91.00	$O_1$6; $O_2$23
2	92.57	$O_1$24; $O_2$8
1	94.20	$O_2$24
2	95.70	$O_2$7
1	97.38	$O_1$25; $O_2$25
2	98.99	$O_2$6
2	33601.19	$O_1$26; $O_2$5
10	05.50	$O_1$27; $P_1$6
2?	06.14	$O_2$4, 27; $P_1$7
2	07.01	$P_1$8
3	08.10	$P_1$9
3	09.50	$P_1$10
3	11.16	$P_1$11
5*db*	13.60	$P_1$12; $P_2$6
2	14.20	$P_2$5, 7, 8
4	15.39	$Q_1$3; $P_1$13; $P_2$4, 10
3	16.51	$P_2$3, 11
5	18.26	$Q_1$4; $P_2$12
2	20.40	$Q_1$5; $P_2$13
3	21.41	$P_1$15
5	22.73	$P_2$14
8*db*	24.80	$Q_1$6; $Q_2$2; $P_1$16; $P_2$15; $P_3$11
5*db*	26.16	$Q_2$3
10	28.75	$Q_1$7; $Q_2$4; $P_1$17; $P_3$14; $P_2$16
1	30.12	$Q_2$5
4	32.79	$Q_1$8; $Q_2$6
1*db*?	34.09	$R_1$4; $R_2$2; $P_3$16
1	35.80	$Q_2$7
4	37.15	$Q_1$9; $P_3$17
2	39.10	$R_2$3; $Q_2$8
3*db*	41.27	$Q_1$10; $P_3$18
3	42.41	$Q_3$4
3	43.00	$Q_2$9; $Q_3$5
1	44.52	$R_2$4; $Q_3$6
1	45.16	$P_2$20
4	46.46	$Q_1$11; $Q_2$10; $Q_3$7; $P_3$19
2	47.70	$R_1$6
3	49.00	$R_2$5
3	49.76	$Q_3$8
10	51.66	$Q_1$12; $Q_2$11; $Q_3$9
1	53.54	$R_3$3
1?	54.14	$R_1$7; $R_2$6
3	55.22	$Q_3$10; $P_3$21
2	56.47	$Q_2$12
3	57.33	$Q_1$13; $R_3$4
4	59.33	$Q_3$11
1	60.36	$R_2$7; $P_3$22
5	61.67	$R_1$8; $Q_2$13; $R_3$5
8	63.41	$Q_1$14; $Q_3$12
3	66.24	$R_3$6; $P_3$23
2	67.36	$R_2$8; $Q_2$14
3	68.33	$R_1$9; $Q_3$13
3	69.43	$Q_1$15
2	71.49	$R_3$7
1	33672.58	$P_3$24
5*db*	73.59	$Q_2$15; $Q_3$14
1	75.15	$R_2$9
2	76.14	$R_1$10; $Q_1$16; $R_3$8
3	79.31	$Q_3$15
2	79.72	$Q_2$16; $P_3$25
1	82.56	$R_2$10; $R_3$9
5	83.22	$Q_1$17
3	85.37	$R_1$11; $Q_3$16
3	86.57	$Q_2$17; $P_3$26
10*D*	90.46	$Q_1$18; $R_2$11; $R_3$10
2	91.94	$Q_3$17
3	93.83	$R_1$12; $Q_2$18
2	94.31	$P_3$27
2	97.13	$R_3$11
4	98.26	$Q_1$19; $R_2$12
4	98.88	$Q_3$18
5*db*	33701.63	$R_1$13; $Q_2$19
2	04.72	$R_3$12
5	06.46	$Q_1$20; $R_2$13; $Q_3$19
4	09.60	$Q_2$20
2	11.01	$R_1$14
2	12.74	$R_3$13
3	14.08	$Q_3$20
2	15.08	$Q_1$21
2	16.18	$R_2$14
3	17.81	$Q_2$21
2	21.13	$R_1$15; $R_3$14
3	22.39	$Q_3$21
2	23.92	$Q_1$22
3*D*	25.25	$R_2$15
2	26.67	$Q_2$22
2	30.21	$R_3$15
2	30.79	$R_1$16; $Q_3$22
2	33.25	$Q_1$23
1	34.48	$R_2$16
3	35.79	$Q_2$23
4*db*	39.62	$R_3$16; $Q_3$23
2	40.68	$R_1$17
3	42.92	$Q_1$24
3	45.42	$R_2$17; $Q_2$24
3	49.20	$R_3$17; $Q_3$24
1	51.12	$R_1$18
3	52.96	$Q_1$25
5	55.34	$R_2$18; $Q_2$25
3	59.22	$R_3$18; $Q_3$25
1	62.05	$R_1$19
2	63.42	$Q_1$26
4	65.87	$R_2$19; $Q_2$26
5*db*	69.69	$R_3$19; $Q_3$26
3	73.49	$R_1$20
3	74.08	$Q_1$27
5*db*	76.82	$R_2$20; $Q_2$27
3	80.04	$Q_3$27
3	80.85	$R_3$20
5	85.32	$R_1$21; $Q_1$28
2	87.65	$Q_3$28
2*db*	88.63	$R_2$21
3	91.11	$Q_3$28
3	92.37	$R_3$21
3	97.19	$R_1$22; $Q_1$29
2	99.19	$Q_2$29
2	33800.61	$R_2$21
2	02.56	$Q_3$29
2	04.00	$R_3$22
3*D*	09.37	$R_1$23; $Q_1$30
2*D*	11.13	$Q_2$30
2	13.04	$R_2$23
2	14.33	$Q_3$30
2	16.24	$R_3$23
2	21.56	$Q_1$31
1	22.49	$R_1$24
2	23.46	$Q_3$31
2	25.68	$R_2$24
3	26.59	$Q_3$31
2	28.87	$R_3$24
2	34.35	$Q_1$32
3	36.04	$R_1$25; $Q_2$32
3	39.07	$R_2$25; $Q_3$32
2*D*	42.32	$R_3$25
3*D*	47.85	$Q_1$33
3	49.41	$R_1$26; $Q_2$33
4	52.41	$R_2$26; $Q_3$33
1	55.28	$R_3$26

TABLE II. *Molecular constants of the upper* ($^3\Sigma$) *and lower* ($^3\Pi$) *electronic states of the* BF *A-system bands.*

	B_v (cm^{-1})	D_v (cm^{-1})	α (cm^{-1})	I_e (g cm^2 $\times 10^{40}$)	r_e cm $\times 10^8$
$v'=0$	1.6235	-4.2×10^{-6}	0.025	16.93	1.220
1	1.6030	-9.7×10^{-6}			
$v''=0$	1.4030		0.0179	19.56	1.312
1	1.3851				
2	1.3672*				

* Extrapolated.

line fitted to the data gives $B_2''=1.3770$. The former value seems too low and the latter too high. The value 1.3672 included in Table II is that obtained from the equation $B_v=B_e+\alpha(v+\frac{1}{2})$ where α is determined from $B_0''-B_1''$.

The constants for the $^3\Sigma$ state have been obtained graphically in the following manner. If $T(K)$ represents the total energy of the rotational energy level, then

$$\Delta_1 F_i(K+\tfrac{1}{2})=T_i(K+1)-T_i(K)$$
$$=R_i(K)-Q_i(K)\pm\delta_{AB}$$

where δ_{AB} represents the Λ-type splitting. Since the $^3\Sigma$ states may be represented by the equations of Hund's case *b*, we have

$$\Delta_1 F_i(K+\tfrac{1}{2})=2B'(K+1)+4D'(K+1)^3+\cdots.$$

Averaging over the three sub-states gives:

$$[\Sigma_i \Delta_1 F_i(K+\tfrac{1}{2})]/[6(K+1)]$$
$$=B'+2D'(K+1)^2+\cdots.$$

Neglecting the Λ-type splitting we have

$$\Sigma_i[R_i(K)-Q_i(K)]/6(K+1)$$
$$=B'+2D'(K+1)^2+\cdots.$$

The left side of this equation, evaluated experimentally, has been plotted against $(K+1)^2$. The intercept of the straight line obtained has been taken as the value of B' and the slope as $2D'$. The value of B' for $v'=0$ is the average of the values obtained from the (0,0), (0,1) and (0,2) bands. The value for $v'=1$ is obtained from the (1,0) band. These values are given in Table II.

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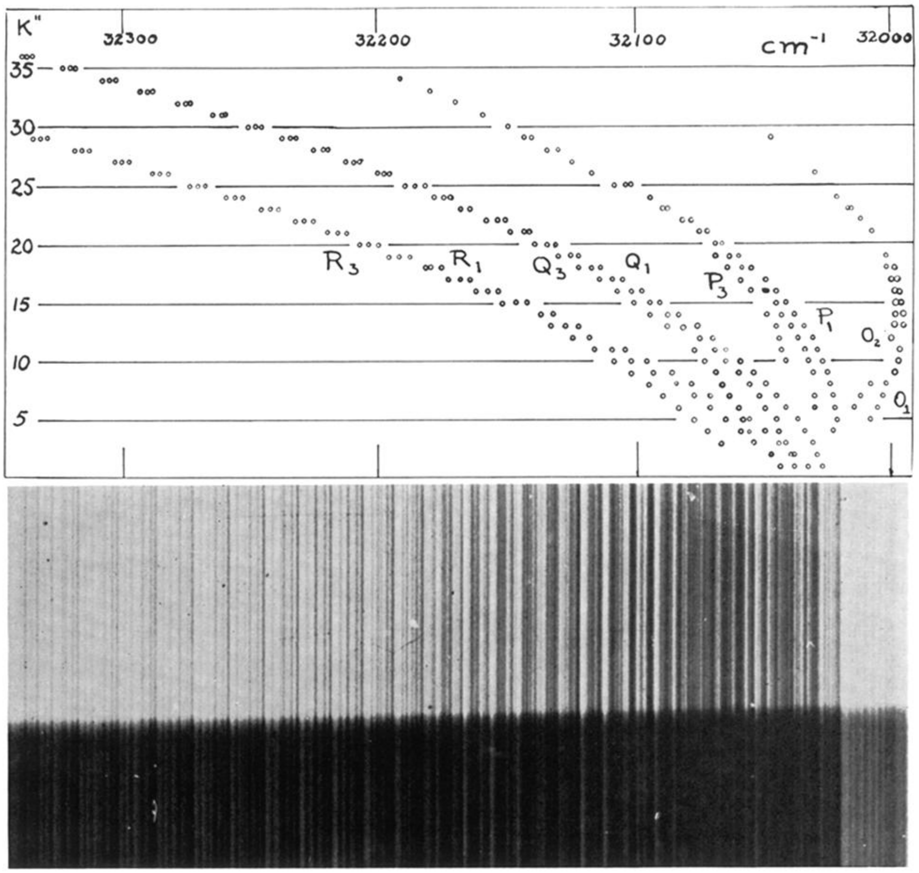

FIG. 1. Fortrat diagram and an enlargement of a part of the (0,0) band of the $^3\Sigma\rightarrow{}^3\Pi$ system of BF. The points are the identified members of the branches and are placed directly above the line so identified.