

FINE STRUCTURE OF THE VISIBLE ABSORPTION BANDS OF BROMINE

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ABSTRACT

A group of bands (from $v'=7$ to $v'=13$, $v''=2, 3$ and 4) in the main absorption band system of bromine ($\text{Br}_2^{79,81}$) have been analyzed and found to consist of P and R branches only. Branches of the less abundant molecules, Br_2^{79} and Br_2^{81} , showing alternating intensities, have been identified in several cases but owing to insufficient resolution a quantitative determination of the ratio of intensities has not been possible. An accurate calculation of the vibrational isotope shift of band origins has confirmed the quantum numbering previously deduced by the writer from measurements of band heads. The numerical values of the vibrational constants have been revised slightly from data on band origins. The analysis gave the following rotational constants for the $\text{Br}_2^{79,81}$ molecule:

$$\begin{array}{ll} B_e'' = 0.08091 & B_e' = 0.0596 \\ \alpha_e'' = 0.00028 & \alpha_e' = 0.00062 \\ I_e'' = 342.1 \times 10^{-40} & I_e' = 465 \times 10^{-40} \\ r_e'' = 2.28 \times 10^{-8} & r_e' = 2.65 \times 10^{-8} \end{array}$$

INTRODUCTION

THE analysis of the visible absorption bands of iodine and chlorine has made it possible to predict with reasonable certainty that the corresponding bands of bromine have the same simple structure, namely, P and R branches only. Nevertheless this spectrum up to the present has defied analysis,¹ for in spite of the smaller atomic weight the bands are more complicated in appearance than those of iodine. This complex appearance is due primarily to the unique isotope situation. The two equally abundant atomic isotopes,² 79 and 81, giving rise to three molecular isotopes, $\text{Br}_2^{79,79}$, $\text{Br}_2^{79,81}$ and $\text{Br}_2^{81,81}$ in the relative abundance 1:2:1. The relative masses are such that the vibrational isotope shifts are small so that each band in the spectrum is made up of a superposition of three bands each having one P and one R branch.

The vibrational analysis of these bands was first studied by Kuhn.³ Recently the vibrational isotope shift of band heads was observed by the writer⁴ and used to establish the quantum numbering. In the latter work a second and weaker band system lying in the extreme red was observed. The extreme red bands, important for the development of theory of the electronic states of the halogens,⁵ have not yet been analyzed.

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¹ M. Hay, J. Franklin Inst. **208**, 363 (1929). The dispersion employed in this work was insufficient to resolve the $P-R$ doubling.

² F. W. Aston, Proc. Roy. Soc. **115**, 487 (1927), gives 78.929 and 80.926 for the isotope masses. Chemical atomic weight 79.92.

³ H. Kuhn, Zeits. f. Physik **39**, 77 (1926).

⁴ W. G. Brown, Phys. Rev. **38**, 1179 (1931).

⁵ R. S. Mulliken, Phys. Rev. **36**, 669, 1440 (1930).

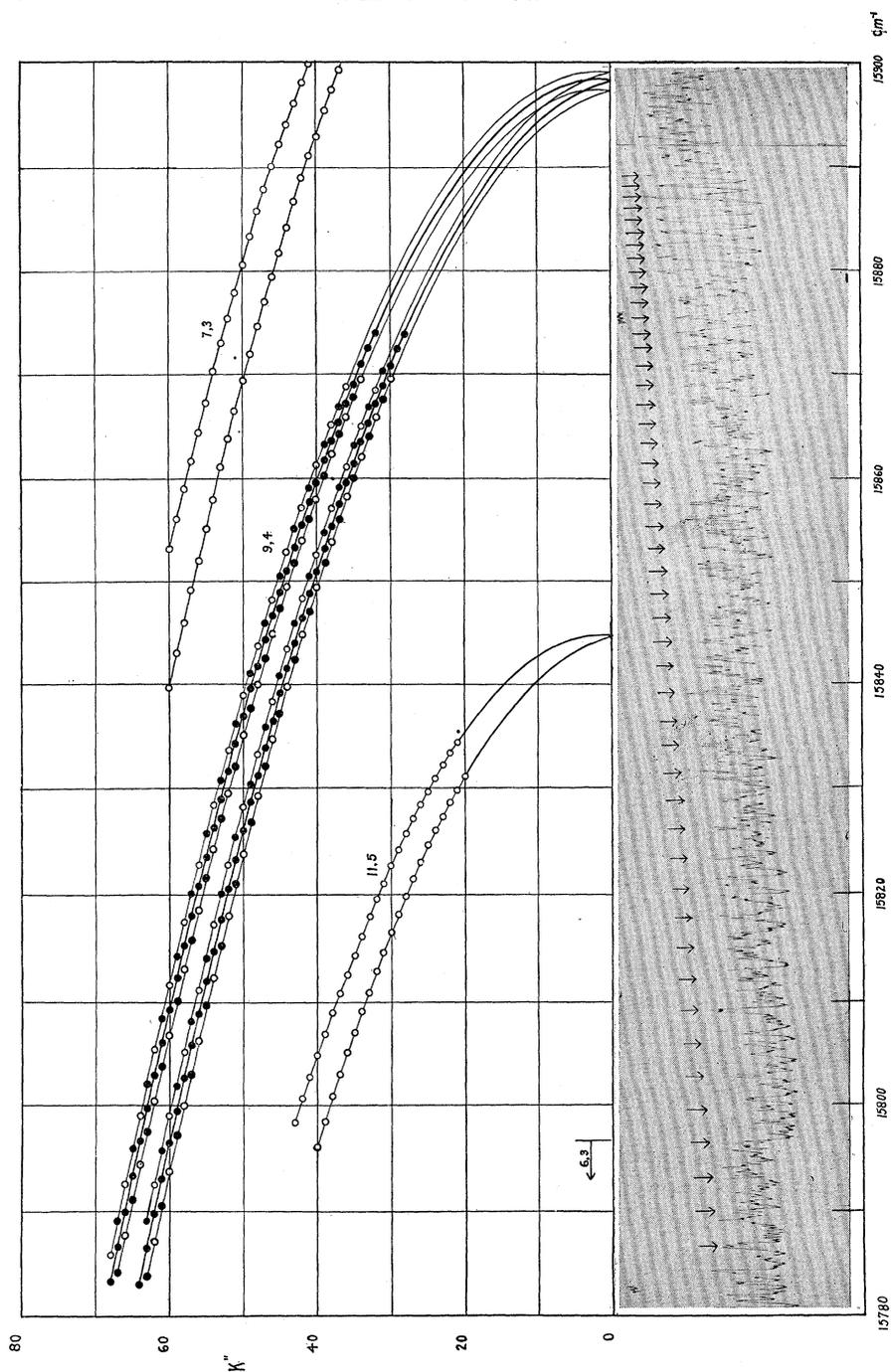


Fig. 1. Fortrat diagram showing the six branches of the 9,4 band but only the $\text{Br}_2^{79,81}$ branches of the weaker overlapping bands, 11,5, and 7,3. The arrows indicate the $P-R$ doublets of $\text{Br}_2^{79,81}$ (9,4). Alternating intensities are indicated by light and dark circles.

EXPERIMENTAL

The photographs were taken in the third order of a 21 ft. Rowland grating (0.8A/mm) on Ilford Special Rapid Panchromatic Plates with neon lines as standards. Two Pyrex absorption tubes, 50 and 150 cm in length were used, the longer tube for the weaker bands in the red. The lines are quite sensitive to pressure broadening and it was found necessary to employ vapor pressures of less than 100 mm to obtain satisfactory resolution. With a single filament 120 watt tungsten lamp exposures from six to twelve hours sufficed depending on the vapor pressure.⁶ No particular precautions were taken to ensure purity of the bromine beyond two fractional distillations of reagent quality bromine in vacuum.

The measurements were reduced directly to wave numbers in vacuum by linear interpolation over intervals of 5 mm on the plate, a polynomial fitting wave-lengths of the standard lines being used to calculate frequencies for each 5 mm. For this time saving method of reduction the writer is indebted to Dr. W. Weizel. In the region 6000–6300A approximately 2,500 lines were measured.

In most cases the *P* and *R* branches of Br₂^{79,81} were readily recognizable because of their slightly greater intensity and absence of alternation. Extensive use was made of the scheme devised by Loomis and Wood⁷ for locating branches of the less abundant molecules. A characteristic feature of these bands is that the *P* and *R* branches of each molecule are coincident or form a series of close doublets over their entire course, *P*(*J*) being coincident with or close to *R*(*J*+4). The separation of these lines decreases with decreasing quantum number and in no case was it possible to resolve them for *P*(*J*) < 18. In one case (9,2) they appear to be exactly coincident up to at least *J* = 60 forming a single series of remarkably sharp lines. In some bands, 10,4 and 9,3, the coincidence is not exact and results in broadening or smearing of lines. This so-called *P*-*R* doubling, of no theoretical significance, arises merely from the particular values of the constants and is characteristic also of the corresponding chlorine and certain of the iodine bands.

CALCULATION OF ROTATIONAL CONSTANTS

The combination differences needed for calculating rotational constants are $R(J) - P(J) = \Delta_2 F'(J)$ and $R(J-1) - P(J+1) = \Delta_2'' F(J)$. These are listed (for Br₂^{79,81}) in Tables Ia and Ib so as to allow comparison of data for each vibrational level. The agreement is satisfactory in all cases where the *P*-*R* doubling has been resolved. Fortunately, in this case the calculation of the constants *B*' and *B*'' from the combination differences is an extremely simple one since they are given by

$$\Delta_2 F = 2B + 4BJ + 8DJ^3$$

where the coefficient *D* is so small for both upper and lower states that one

⁶ Weak continuous absorption overlaps the main absorption bands. Note the gradually changing background density in the microphotometer trace in Fig. 1.

⁷ F. W. Loomis and R. W. Wood, Phys. Rev. **32**, 223 (1928).

TABLE IA. Combination differences for the lower levels of $\text{Br}_2^{79,81}$.
 $\Delta_2 F'' = R(J-1) - P(J+1)$

J	8,2	9,2	10,2	7,3	8,3	10,3	11,3	12,3	13,3	9,4	10,4	11,4
20		6.52			6.55							
21		6.83			6.94							
22		7.18			7.17							
23		7.51			7.51		7.51	7.53			7.55	
24	7.80	7.84			7.81		7.87	7.80	7.83		7.85	7.84
25	8.20	8.17			8.11		8.22	8.14	8.17		8.19	8.08
26	8.49	8.49			8.38		8.45	8.56	8.47		8.53	8.44
27	8.86	8.83	8.84		8.72		8.75	8.79	8.78		8.74	8.75
28	9.11	9.15	9.13		9.10		9.18	9.12	9.09		9.05	9.06
29	9.45	9.48	9.42		9.41		9.46	9.42	9.44		9.40	9.48
30	9.78	9.80	9.83		9.72		9.74	9.80	9.70		9.71	9.77
31	10.07	10.11	10.07		10.06		10.10	10.08	10.02		9.97	10.07
32	10.42	10.42	10.42		10.29		10.43	10.38	10.37		10.30	10.41
33	10.77	10.73	10.72		10.72		10.78	10.69	10.67	10.71	10.74	10.73
34	10.98	11.04	11.07		11.00		11.07	11.07	11.05	11.02	11.04	11.03
35	11.30	11.36	11.39		11.36	11.32	11.37	11.32	11.39	11.36	11.35	11.36
36	11.69	11.68	11.68		11.68	11.65	11.68	11.65	11.71	11.66	11.67	11.70
37	12.10	12.01	12.02		11.97	12.00	12.00	12.03	12.03	11.97	12.02	11.96
38	12.33	12.32	12.38		12.31	12.29	12.31	12.29	12.33	12.26	12.34	12.24
39	12.62	12.64	12.70		12.51	12.61	12.62	12.58	12.68	12.58	12.67	12.57
40	13.01	12.98	12.99		12.90	12.94	12.95	12.97	12.96	12.88	12.97	12.79
41		13.30	13.31		13.22	13.24	13.28	13.31	13.25	13.23	13.27	13.23
42		13.62	13.62		13.65	13.55	13.62	13.58	13.56	13.52	13.59	13.51
43		13.93	13.92		13.83	13.88	13.86	13.97	13.89	13.86	13.94	13.84
44		14.25	14.28			14.23	14.20	14.19	14.24	14.20	14.18	
45		14.60	14.61			14.60	14.56	14.50	14.52	14.45	14.49	
46		14.91	14.92			14.87	14.88	14.82	14.87	14.85	14.83	
47		15.23	15.24				15.24	15.20	15.20	15.09	15.20	
48		15.55	15.67					15.55		15.43	15.53	
49		15.88	15.88					15.82		15.73	15.78	
50		16.22	16.23					16.13		15.96	16.19	
51		16.52						16.41		16.40		
52		16.83						16.80		16.66		
53		17.15								16.97		
54		17.46								17.33		
55		17.77		17.77						17.64		
56				18.06						17.99		
57				18.36						18.37		
58				18.67						18.64		
59				18.99						18.88		
60				19.33						19.24		
61				19.61								
B'' obs.	0.08010	0.08017	0.08023	0.07998	0.07975	0.07988	0.08007	0.07995	0.07997	0.07967	0.08000	0.07975
B'' calc.	0.08022				0.07995					0.07967		

can use the theoretical value ($D_e = -4B_e^3/\omega_e^2$). The value of B is then obtained from the expression

$$B = \frac{\Sigma(\Delta_2 F + 8DJ^3)}{4\Sigma(J + \frac{1}{2})}$$

The values so obtained are shown in Table I together with the values calculated from an expression of the type

$$B_v = B_e - \alpha(v + \frac{1}{2}).$$

THE ISOTOPE EFFECT

The lines of the v', v'' band of $\text{Br}_2^{79,81}$ can be represented by the equation

$$\nu = \nu^0 + B_{v'}(J' + \frac{1}{2})^2 + D_{v'}(J' + \frac{1}{2})^4 - B_{v''}(J'' + \frac{1}{2})^2 - D_{v''}(J'' + \frac{1}{2})^4 \quad (1)$$

where the coefficients B_v and D_v are functions of the vibrational quantum numbers v' and v''

$$B_v = B_e - \alpha(v + \frac{1}{2}) \quad (2)$$

$$D_v = D_e + \beta(v + \frac{1}{2}). \quad (3)$$

TABLE IB. Combination differences for the upper levels of Br₂^{79,81}.
 $\Delta_2R^J = R(J) - P(J)$

J	7,3	8,2	8,3	9,2	9,4	10,2	10,3	10,4	11,3	11,4	12,3	13,3
22			4.91									
23		5.08	5.06	5.02				5.04	4.95	4.98	4.85	4.75
24		5.35	5.32	5.17				5.24	5.20	5.10	5.06	4.94
25		5.51	5.45	5.45				5.44	5.35	5.32	5.31	5.22
26		5.78	5.65	5.71		5.62		5.69	5.54	5.52	5.48	5.40
27		5.98	5.94	5.86		5.83		5.90	5.78	5.75	5.73	5.59
28		6.17	6.15	6.12		6.04		6.00	5.93	5.97	5.89	5.83
29		6.34	6.37	6.33		6.27		6.24	6.21	6.15	6.11	5.95
30		6.60	6.62	6.46		6.40		6.45	6.44	6.48	6.27	6.16
31		6.77	6.71	6.73		6.66		6.62	6.63	6.70	6.53	6.41
32		6.99	7.03	6.94	6.99	6.84		6.92	6.86	6.86	6.70	6.60
33		7.29	7.23	7.16	7.21	7.09		7.15	7.05	7.08	6.91	6.82
34		7.52	7.48	7.35	7.41	7.28	7.30	7.34	7.28	7.29	7.13	7.04
35		7.60	7.68	7.57	7.65	7.48	7.50	7.57	7.47	7.48	7.33	7.29
36		7.85	7.91	7.77	7.89	7.74	7.73	7.83	7.60	7.64	7.55	7.48
37		8.09	8.16	8.00	8.07	7.96	7.93	7.99	7.81	7.87	7.73	7.66
38		8.39	8.25	8.23	8.25	8.15	8.14	8.20	8.07	8.09	7.92	7.88
39		8.58	8.53	8.43	8.44	8.37	8.34	8.45	8.28	8.21	8.14	8.06
40		8.73	8.74	8.75	8.69	8.54	8.56	8.66	8.47	8.46	8.35	8.27
41		8.93	8.99	8.87	8.86	8.78	8.77	8.87	8.69	8.62	8.56	8.45
42			9.16	9.03	9.12	9.02	8.95	9.08	8.90	8.88	8.79	8.63
43			9.50	9.32	9.36	9.18	9.19	9.24	9.08	9.06	9.00	8.83
44				9.45	9.51	9.36	9.44	9.47	9.26	9.31	9.16	9.03
45				9.69	9.75	9.63	9.65	9.66	9.49		9.34	9.31
46				9.99	9.93	9.88	9.86	9.88	9.75		9.60	9.47
47				10.09	10.20	10.05	10.06	10.11	9.93		9.82	9.63
48				10.41	10.35	10.27		10.34	10.16		10.03	9.87
49				10.67	10.56	10.57		10.59			10.19	
50				10.77	10.81	10.61		10.76			10.34	
51				11.05	11.01	10.90		11.02			10.59	
52				11.20	11.20						10.81	
53				11.36	11.41						11.04	
54	11.91			11.70	11.60							
55	12.14			11.86	11.87							
56	12.39			12.03	12.12							
57	12.58			12.32	12.30							
58	12.77				12.49							
59	12.99				12.73							
60	13.20				12.88							
61	13.45				13.13							
62	13.62											
B' obs.	0.05487		0.05415		0.05367		0.05303		0.05250		0.05170	
		0.05412		0.05355		0.05297			0.05252		0.05100	
B' calc.	0.05487		0.05425		0.05362		0.05300		0.05237		0.05175	0.05112

The general theory⁸ of the isotope effect in band spectra indicates that for an isotope molecule one substitutes $\rho(v + \frac{1}{2})$ for $(v + \frac{1}{2})$ and $\rho(J + \frac{1}{2})$ for $(J + \frac{1}{2})$ where ρ is the square root of the ratio of the reduced masses. ν° is also a function of the vibrational quantum numbers and so the isotope molecule will have a different origin, $\nu^\circ + \delta\nu^\circ$. $\delta\nu^\circ$ is the vibrational isotope effect and can be treated separately. Then on making these substitutions one finds that for the isotope molecule, such as Br₂⁷⁹ or Br₂⁸¹, one obtains new coefficients in equation (1) related to the original ones as follows:

$${}^iB_v = [B_e - \alpha\rho(v + \frac{1}{2})]\rho^2 \tag{4}$$

$${}^iD_v = [D_e + \beta\rho(v + \frac{1}{2})]\rho^4. \tag{5}$$

In table II the combination differences for Br₂⁷⁹ and Br₂⁸¹ are given together with the B values calculated from them, and those calculated from the data for Br₂^{79,81} by means of equation (4). The values of ρ calculated from Aston's² atomic weights, are 1.00623 and 0.99373 for Br₂⁷⁹ and Br₂⁸¹ respectively.

Substituting appropriate values for the constants in equation (1) one can calculate from each band line a value of ν° . The origins calculated from Br₂⁷⁹

⁸ R. S. Mulliken, Phys. Rev. 25, 119 (1925).

or Br_2^{81} lines will differ from the corresponding $\text{Br}_2^{79,81}$ origins by an amount, $\delta\nu^0$ which is given theoretically by

$$\begin{aligned} \delta\nu^0 = & \omega_e'(v' + \frac{1}{2})(\rho - 1) - \omega_e'x_e'(v' + \frac{1}{2})^2(\rho^2 - 1) + \dots \\ & - \omega_e''(v'' + \frac{1}{2})(\rho - 1) + \omega_e''x_e''(v'' + \frac{1}{2})^2(\rho^2 - 1) - \dots \end{aligned} \quad (6)$$

where the vibrational constants ω_e and x_e to be used are those for $\text{Br}_2^{79,81}$ and the appropriate values of ρ are to be substituted to obtain the shift of the

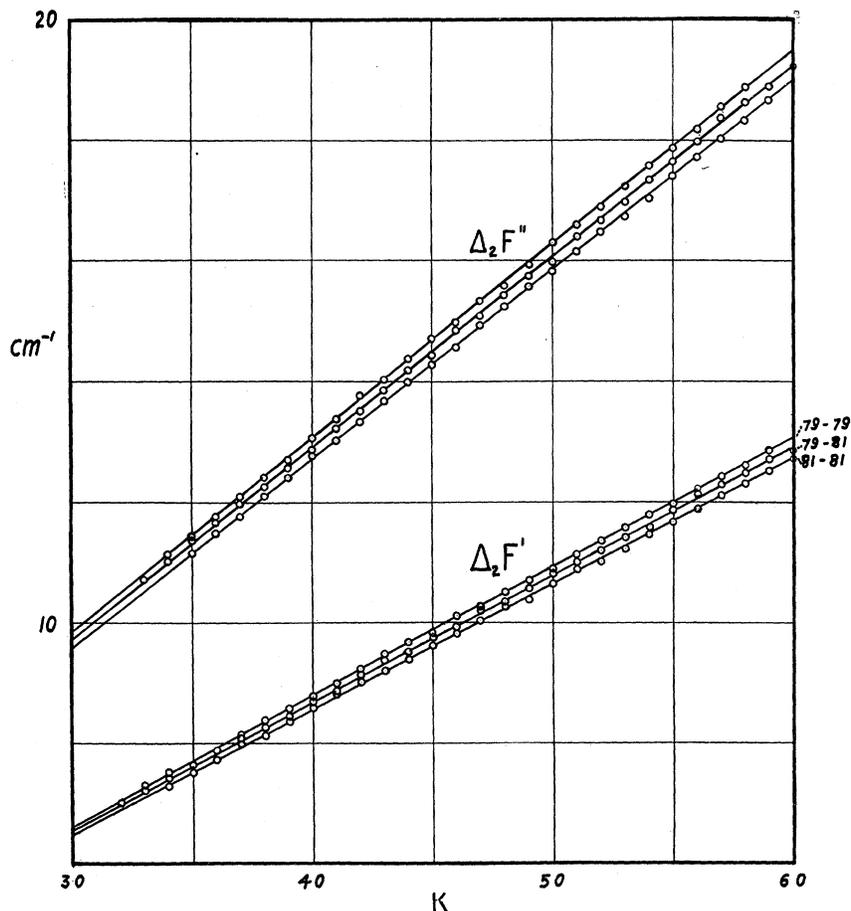


Fig. 2. Combination differences for the 9,4 band.

Br_2^{79} or Br_2^{81} origin relative to that of $\text{Br}_2^{79,81}$. In this case terms involving $(v + \frac{1}{2})^3$ are negligible. Table III gives the vibrational analysis together with the vibrational constants of $\text{Br}_2^{79,81}$, and in Table IV the "observed" vibrational isotope shifts of Br_2^{79} and Br_2^{81} , and the values of $\delta\nu^0$ calculated from equation (6) are given. The agreement is well within the limit of error of the constants used and confirms the vibrational numbering. This is also shown by Fig. 4 where the quantity $\Delta v(\Delta v = \delta G'/\omega_v)$ is plotted against $(v' + \frac{1}{2})$ (cf. Fig. 1 reference 4).

An alternative method of calculating the vibrational isotope shift from the band lines is to consider the separation of corresponding lines as the sum of the vibrational isotope shift, $\delta\nu^0$, and a rotational shift given by

$$\delta\nu_{\text{rot}} = - ({}^iB' - B' + {}^iB'' - B'') J'' + ({}^iB' - B' - {}^iB'' + B'') J''^2$$

for *P* lines, and

$$\delta\nu_{\text{rot}} = ({}^iB' - B' + {}^iB'' - B'')(J'' + 1) + ({}^iB' - B' - {}^iB'' + B'')(J'' + 1)^2$$

for *R* lines.

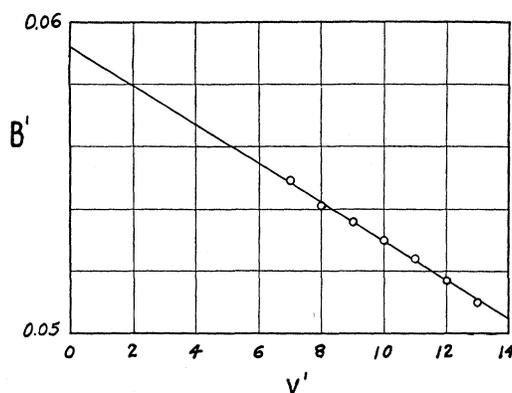


Fig. 3.

TABLE II. Combination differences for Br_2^{79} and Br_2^{81} .

<i>J</i>	9,4				10,2				11,3			
	Δ_2F'' 79-79	Δ_2F'' 81-81	Δ_2F' 79-79	Δ_2F' 81-81	Δ_2F'' 79-79	Δ_2F'' 81-81	Δ_2F' 79-79	Δ_2F' 81-81	Δ_2F'' 79-79	Δ_2F'' 81-81	Δ_2F' 79-79	Δ_2F' 81-81
33			7.30									
34	11.15		7.51	7.28			7.34	7.16		10.58		6.97
35	11.42	11.15	7.68	7.50	11.49	11.26	7.57	7.42		10.92		7.08
36	11.76	11.49	7.87	7.72	11.82	11.56	7.83	7.62	11.81	11.50		7.33
37	12.09	11.76	8.14	7.98	12.29	11.91	8.02	7.84	12.13	11.84	7.95	7.55
38	12.41	12.10	8.36	8.12	12.48	12.20	8.38	8.13	12.50	12.19	8.15	7.81
39	12.71	12.41	8.57	8.35	12.92	12.53	8.47	8.28	12.76	12.54	8.37	7.99
40	13.06	12.77	8.77	8.58	13.18	12.84	8.72	8.46	13.07	12.72	8.54	8.10
41	13.38	13.04	8.98	8.81			8.86	8.66	13.45	13.01	8.77	8.33
42	13.68	13.34	9.22	9.00					13.71	13.41	9.00	8.53
43	14.04	13.68	9.47	9.19					14.03	13.72	9.14	8.78
44	14.38	14.00	9.66	9.38								
45	14.71	14.28	9.84	9.61								
46	14.98	14.58	10.11	9.83								
47	15.32	14.94	10.27	10.04								
48	15.59	15.23	10.51	10.26								
49	15.94	15.56	10.71	10.39								
50	16.30	15.81	10.89	10.65								
51	16.58	16.14	11.14	10.89								
52	16.89	16.49	11.36	11.02								
53	17.23	16.73	11.59	11.23								
54	17.57	17.03	11.80	11.47								
55	17.86	17.41	11.99	11.66								
56	18.19	17.72	12.23	11.90								
57	18.56	18.03	12.44	12.11								
58	18.87	18.33	12.63	12.32								
59		18.66	12.88	12.52								
60			12.74									
<i>B</i> obs.	0.08067	0.07855	0.05432	0.05291	0.08129	0.07934	0.05354	0.05238	0.08085	0.07896	0.05298	0.05179
<i>B</i> calc.	0.08066	0.07869	0.05426	0.05299	0.08122	0.07923	0.05362	0.05238	0.08094	0.07896	0.05298	0.05177

TABLE III. *Vibrational analysis of Br₂^{79,81} band origins.*

v' \ v''	2		3		4
7			15,938.36		
			139.11		
8	16,394.24	316.77	16,077.47		
	135.26		135.26		
9	16,529.50	316.77	16,212.73	314.66	15,898.07
	131.49		131.45		131.49
10	16,660.99	316.81	16,344.18	314.62	16,029.56
			127.64		127.65
11			16,471.82	314.61	16,157.21
			123.77		
12			16,595.59		
			119.98		
13			16,715.57		

$$\nu = 15,891.3 + 169.71(v' + \frac{1}{2}) - 1.913(v' + \frac{1}{2})^2 - 323.2(v'' + \frac{1}{2}) + 1.07(v + \frac{1}{2})^2$$

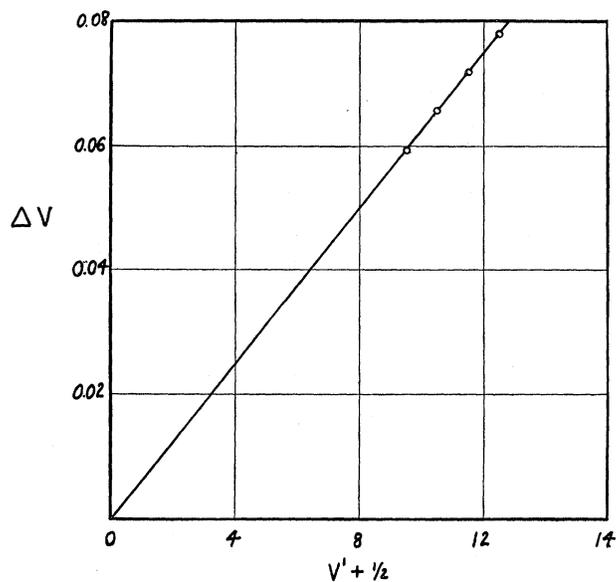


Fig. 4.

TABLE IV. *Observed and calculated vibrational isotope shifts.*

Band	Mol.	Origin	$\delta\nu^\circ$ Obs.	$\delta\nu^\circ$ Calc.
10,2	79-79	16,664.51	+3.52	+3.52
	79-81	660.99		
	81-81	657.43	-3.56	-3.56
11,3	79-79	16,473.97	+2.15	+2.10
	79-81	471.82		
	81-81	469.68	-2.14	-2.16
9,4	79-79	15,897.17	-0.90	-0.90
	79-81	898.07		
	81-81	898.97	+0.90	+0.90
12,3	79-79	16,598.20	+2.61	+2.59
	79-81	595.59		

The difference in D values for the two molecules is negligible. Values of $\delta\nu^\circ$ calculated in this way for each observed line in the $9,4$ band are given in Table V. For some reason the R branch of $\text{Br}_2^{79,79}$ gives a value slightly low but the other values are in extremely good agreement with theory.

ALTERNATING INTENSITIES

One of the most interesting questions in connection with the spectrum of bromine is that of the nuclear spins and its effect on the intensities of lines in bands of the symmetrical molecules. Unfortunately this question cannot be answered at present any more than to state that the phenomenon of alternating intensities is definitely observable. This is shown by the intensities given in Table V which are peak height in mm on the microphotometer trace of the $9,4$ band reproduced in Fig. 1, the lines originating on odd numbered levels (odd J'') being stronger. Thus the complete wave-function ψ must be anti-symmetric in the nuclei, and, like Cl, the Br nuclei obey the Fermi-Dirac statistics in accordance with the usual rule for atoms containing odd numbers of protons. In many respects this is the simplest region of the spectrum yet

TABLE V. Lines and isotope shifts in the $9,4$ band, P branches.

J''	Int.	81, 81	Int.	79, 81	Int.	79, 79	$\delta\nu$	$\delta\nu^0$	$\delta\nu$	$\delta\nu^0$
29				15872.24		15871.00			1.24	0.90
30		15871.83	30	870.56	12	869.30	1.27	0.91	1.26	0.90
31	20	870.09	29	868.83	27	867.51	1.26	0.87	1.32	0.93
32	14	868.36	24	867.09	16	865.75	1.27	0.86	1.34	0.93
33	18	866.59	21	865.23	14	863.90	1.36	0.92	1.33	0.89
34	15	864.74	27	863.37	16	861.98	1.37	0.91	1.39	0.93
35	13	862.82	20	861.42	18	860.06	1.40	0.91	1.36	0.87
36	17	860.87	21	859.42	21	858.07	1.45	0.94	1.35	0.84
37	18	858.83	29	857.41	30	855.98	1.42	0.88	1.43	0.89
38	10	856.83	20	855.34	16	853.85	1.49	0.92	1.49	0.92
39	23	854.71	25	853.22	27	851.71	1.49	0.89	1.51	0.91
40	7	852.54	21	851.01	13	849.50	1.53	0.90	1.51	0.88
41	19	850.29	27	848.78	19	847.22	1.51	0.85	1.56	0.90
42	9	848.08	23	846.47	17	844.89	1.61	0.92	1.58	0.89
43	22	845.76	28	844.12	23	842.52	1.64	0.92	1.60	0.88
44	17	843.40	28	841.73	17	840.07	1.67	0.92	1.66	0.91
45	19	840.95	32	839.28	23	837.61	1.68	0.90	1.67	0.88
46	24	838.50	25	836.79	18	835.02	1.71	0.89	1.77	0.95
47	19	835.98	28	834.18	19	832.47	1.80	0.95	1.71	0.86
48	20	833.39	24	831.63	15	829.81	1.76	0.87	1.82	0.93
49	14	830.79	22	828.95	16	827.15	1.84	0.92	1.80	0.88
50	14	828.09	24	826.25	19	824.38	1.84	0.88	1.87	0.91
51	15	825.37	25	823.45	25	821.56	1.92	0.92	1.89	0.89
52	14	822.60	14	820.66	9	818.71	1.94	0.90	1.95	0.91
53	20	819.77	20	817.80	20	815.81	1.97	0.89	1.99	0.91
54	8	816.89	22	814.90	20	812.84	1.99	0.88	2.06	0.94
55	19	813.97	19	811.88	14	809.83	2.09	0.94	2.05	0.89
56		810.92		808.86		806.78	2.06	0.86	2.08	0.88
57		807.91		805.76		803.63	2.15	0.91	2.13	0.89
58		804.82		802.61		800.45	2.21	0.93	2.16	0.88
59		801.69		799.42		797.20	2.27	0.95	2.22	0.90
60		798.48		796.22			2.26	0.89		
61				792.91						
							Mean	0.903		0.899—
							Theoretical	0.896		0.902—

TABLE V. (Continued. *R* branches).

<i>J</i>	Int. 81,81	Int. 79,81	Int. 79,79	$\delta\nu$	$\delta\nu^0$	$\delta\nu$	$\delta\nu^0$
32		15874.08					
33		872.44	15871.20			1.24	0.88
34	15872.02	27 870.78	10 869.49	1.24	0.86	1.29	0.91
35	27 870.32	28 869.07	24 867.74	1.25	0.84	1.33	0.92
36	19 868.59	28 867.31	19 865.94	1.28	0.85	1.37	0.94
37	19 866.81	21 865.48	15 864.12	1.33	0.88	1.36	0.90
38	20 864.95	26 863.59	14 862.21	1.36	0.88	1.38	0.90
39	24 863.06	26 861.66	24 860.28	1.40	0.89	1.38	0.87
40	8 861.12	16 859.70	16 858.27	1.42	0.88	1.43	0.89
41	16 859.10	29 857.64	23 856.20	1.46	0.90	1.44	0.87
42	9 857.08	25 855.59	12 854.11	1.49	0.90	1.48	0.89
43	23 854.95	31 853.48	24 851.99	1.47	0.85	1.49	0.87
44	12 852.78	27 851.24	13 849.73	1.54	0.89	1.51	0.86
45	23 850.56	33 849.03	21 847.45	1.53	0.85	1.58	0.90
46	13 848.33	24 846.72	11 845.13	1.61	0.90	1.59	0.88
47	25 846.02	27 844.38	25 842.74	1.64	0.90	1.64	0.89
48	15 843.65	26 841.98	13 840.32	1.67	0.89	1.66	0.88
49	25 841.18	26 839.51	19 837.86	1.67	0.86	1.65	0.84
50	17 838.74	23 837.06	17 835.27	1.68	0.83	1.79	0.94
51	23 836.26	28 834.46	23 832.70	1.80	0.91	1.76	0.88
52	19 833.62	29 831.87	19 830.07	1.75	0.83	1.80	0.88
53	14 831.00	23 829.21	19 827.40	1.79	0.84	1.81	0.86
54	14 828.36	25 826.50	16 824.64	1.86	0.87	1.86	0.87
55	12 825.63	18 823.75	20 821.82	1.88	0.85	1.93	0.90
56	16 822.85	21 820.98	9 819.01	1.87	0.80	1.97	0.90
57	24 819.99	25 818.06	22 816.07	1.93	0.82	1.99	0.88
58	5 817.14	19 815.10	17 813.08	2.04	0.89	2.02	0.87
59	17 814.21	18 812.15	12 810.08	2.06	0.87	2.07	0.88
60	811.22	809.10	806.98	2.12	0.89	2.12	0.89
61	808.18	806.04	803.90	2.14	0.87	2.14	0.87
62	805.09	802.88	800.66	2.21	0.90	2.22	0.90
63	801.96	799.70	797.44	2.26	0.90	2.26	0.90
64		796.46					
65		793.17					
				Mean	0.870		0.889
				Theoretical	0.896		0.902

TABLE VI. Rotational constants of bromine.

	Upper State			Lower State			
	79-79	79-81	81-81	79-79	79-81	81-81	
B_e	0.0603	0.0595	0.05882	0.08192	0.08091	0.07990	
B_0	0.0600	0.0592	0.05851	0.08178	0.08077	0.07976	
I_e	459	465	471	337.9	342.1	346.4	$\times 10^{-40}$
I_0	461	467	473	338.5	342.7	347.0	$\times 10^{-40}$
r_e	2.65	2.65	2.65	2.28	2.28	2.28	$\times 10^{-8}$
r_0	2.66	2.66	2.66	2.28	2.28	2.28	$\times 10^{-8}$
D_e	3.0	2.9	2.8	2.0	2.0	2.0	$\times 10^{-8}$
α	0.00064	0.000625	0.00061	0.00028	0.000275	0.00027	

the overlapping by the 11,5 and 7,3 bands is a serious complication. It is of interest to note that the nuclear spin $I=3/2$ as deduced from hyperfine structure⁹ would result in a ratio of intensities 1.67:1. This value is favored by the present rough measurements but the value $I=5/2$ with a ratio of intensities 1.4:1 is not precluded. This problem requires further study.

⁹ DeBruin, Nature **125**, 414 (1930); S. Tolansky, Nature **127**, 855 (1931).

SUMMARY OF CONSTANTS

Values of the rotational constants are given for the three molecules in Table VI. These form an inter-connecting set as the values for the less abundant molecules were calculated from those for $\text{Br}_2^{79,81}$ by means of the various relations given above.

My thanks are due to Professor R. S. Mulliken for suggestions and advice and to Professor G. S. Monk for his cooperation in obtaining best results from the grating.

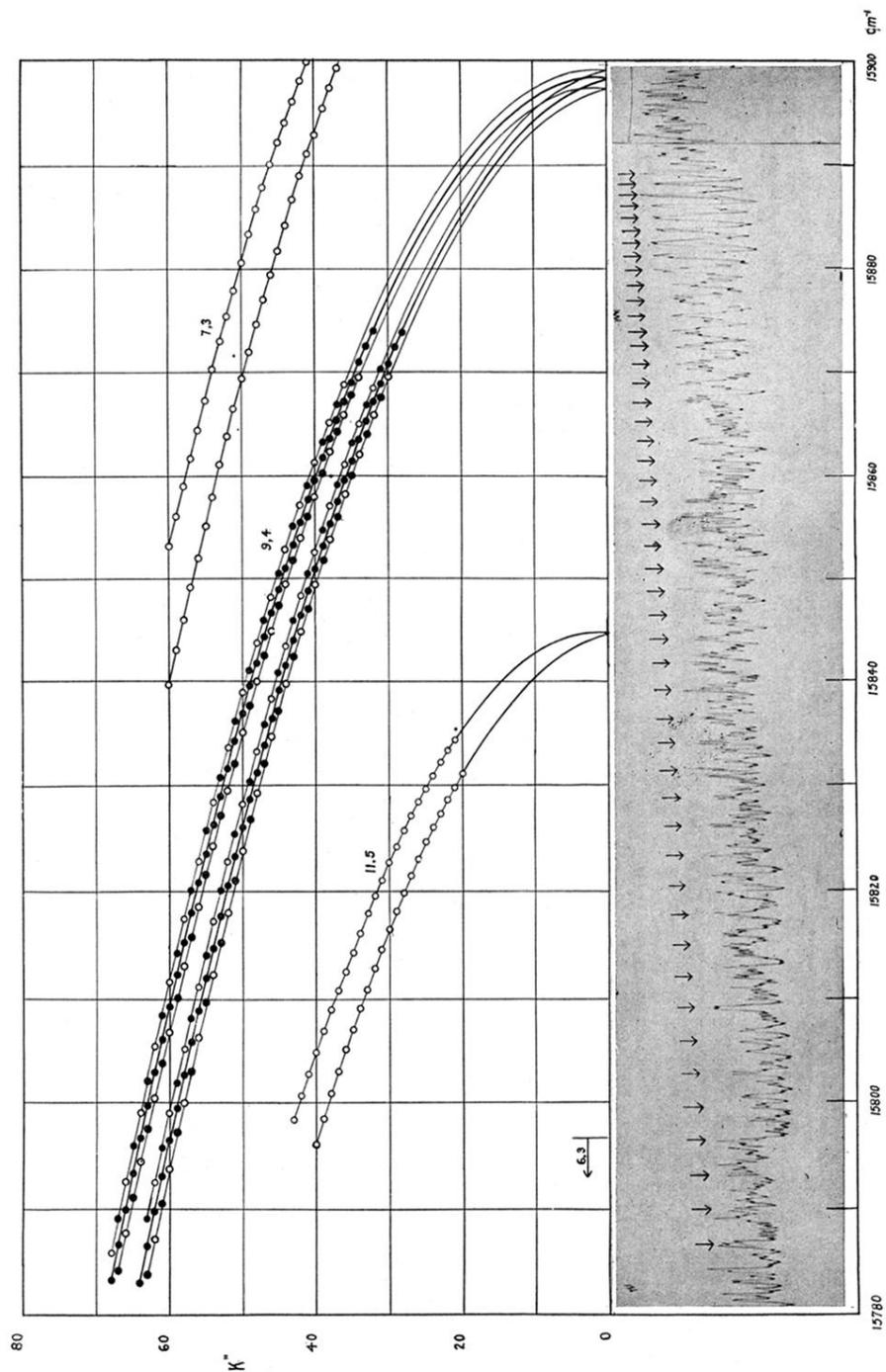


Fig. 1. Fortrat diagram showing the six branches of the 9,4 band but only the $\text{Br}_2^{79,81}$ branches of the weaker overlapping bands, 11,5, and 7,3. The arrows indicate the $P-R$ doublets of $\text{Br}_2^{79,81}$ (9,4). Alternating intensities are indicated by light and dark circles.