

ROTATIONAL STRUCTURE OF THE RED BANDS OF POTASSIUM

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(Received November 6, 1931)

ABSTRACT

A rotational analysis has been made of four bands of the red system of K_2 which had been photographed under high dispersion. The principal molecular constants of the ground state ($^2\Sigma_g^+$) and of the upper state ($^4\Pi_u$) are as follows:

$$\begin{array}{lll} B_0'' = 0.05611 & r_e'' = 3.91 \times 10^{-8} & \alpha'' = 0.000219 \\ B_0' = 0.04812 & r_e' = 4.22 \times 10^{-8} & \alpha' = 0.000235 \end{array}$$

The magnitude of the Λ type doublings of the $^4\Pi$ state agrees with Van Vleck's formula for it. The relationships between the molecular constants show that all rotational levels, with both even and odd values of J , are present. Alternating intensities are observed, the lines with odd J'' being stronger. It is concluded that the nuclear spin of K^{39} is definitely not zero, and that the nucleus obeys the Fermi-Dirac statistics.

THE red absorption bands of diatomic potassium were photographed, with the cooperation of Professor R. W. Wood, primarily with the object of determining whether or not the nuclear spin of the principal isotope, K^{39} , was zero, as had been concluded by two independent observers^{2,3} of the hyperfine structure of arc and spark lines respectively. We were able to report immediately⁴ that an inspection of our plates showed conclusively that this could not be true, for alternating intensities were clearly apparent in the well resolved branches; and moreover the spacing of the lines was such as to preclude the possibility that alternate ones were missing, as they must be if the spin were zero. This latter statement was based on a comparison of the observed spacing with that estimated by extrapolating the known spacings of the corresponding bands of Li_2 and Na_2 .

A rotational analysis of four bands of this spectrum has now been completed and thoroughly checked by the combination relations, with the result that our earlier conclusions are verified, independently of the extrapolation from Li_2 and Na_2 .

As stated in the joint paper,⁴ the spectrum was photographed in absorption in the fourth order of the Tuxedo forty foot spectrograph with a particularly fine seven inch plane grating with 15,000 lines per inch. Sunlight was used as a background and the solar lines as a comparison, their wavelengths being obtained from the revised Rowland's Table.⁵

The red band system of potassium is expected to be, like the green ones of

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² Schüler and Brück, *Zeits. f. Physik* **58**, 735 (1929).

³ Frisch and Kronig, *Naturwiss.* **19**, 444 (1931).

⁴ Loomis and Wood, *Phys. Rev.* **38**, 854 (1931).

⁵ Revision of Rowland's Preliminary Table of Solar Wave-lengths, St. John, Moore, Ware, Adams and Babcock. Published by Carnegie Inst. of Washington (1928).

lithium and sodium, a ${}^1\Pi - {}^1\Sigma$ transition and this is confirmed by the analysis, since each band is found to consist of one P , one Q and one R branch.

The analysis was carried out in much the same way as that⁶ of the green bands of Na_2 . The lines belonging to the branches were found, where possible, by picking out series of regularly spaced lines by inspection and the assignments were checked and completed by the construction of graphs similar to Figs. 2 of the paper on sodium.⁶ In this way three series were found in each band, though there were some regions where two or even three series coalesced. The Q branches could be identified by inspection because of their greater intensity. The P and R branches were identified and triplets of lines with common values of J'' were picked out from them and the Q branches by application of the PQR combination relation

$$R(J'') - Q(J'') \cong Q(J'' + 1) - P(J'' + 1). \quad (1)$$

It is true, of course, that this relation is theoretically not exact, since there is Λ type doubling in the upper state and hence the initial levels for the Q lines differ from those of the P and R lines and there is a "combination defect". In the case of potassium, however, this combination defect is so small that it is barely detectable and the PQR combination relation is quite sufficient for the identification of the lines in the three branches which have common J'' .

The measured frequencies of the lines of the (1, 0) (1, 1) (0, 1) and (0, 2) bands, with the quantum numbers assigned to them, as described below, are given in Table I.

TABLE I. Measured frequencies of band lines.

(1, 0) band		R	J''	(1, 1) band	
P	Q			P	Q
	15438.82		21	15345.08	
	38.45		22	44.63	
	38.08		23	44.14	
15435.34	—		24	43.69	
34.88	37.27		25	43.20	
34.35	36.83		26	42.66	
33.80	36.38		27	42.14	
33.25	35.94		28	41.61	
32.68	35.44		29	—	
32.12	34.95		30	40.47	
31.48	34.45	15437.39	31	39.91	
30.89	33.92	37.09	32	39.28	
30.24	33.39	36.63	33	38.67	15341.84
29.59	32.82	36.17	34	38.00	—
28.90	32.25	35.71	35	37.37	40.75
28.23	31.66	35.22	36	36.70	40.14
27.50	31.05	34.68	37	36.00	39.57
26.80	30.43	34.13	38	—	38.96
26.07	29.78	33.61	39	34.63	38.34
25.32	29.14	33.05	40	33.86	37.71
24.58	28.45	32.46	41	33.13	—
23.77	—	31.86	42	—	36.36
22.97	27.04	31.26	43	31.60	35.69
22.17	26.34	30.70	44	30.82	34.98
21.32	25.60	30.00	45	30.00	34.26

⁶ Loomis and Wood, Phys. Rev. **32**, 223 (1928).

TABLE I. (Continued).

<i>P</i>	(1, 0) band <i>Q</i>	<i>R</i>	<i>J''</i>	<i>P</i>	(1, 1) band <i>Q</i>	<i>R</i>
15420.43	15424.85	15429.36	46	15329.16	15333.54	15338.00
19.60	24.09	28.65	47	28.33	32.80	37.37
18.62	23.30	27.97	48	27.49	32.04	36.70
17.83	22.47	27.23	49	26.60	31.24	36.00
16.90	21.67	26.51	50	25.72	30.45	35.27
15.98	20.80	25.76	51	24.80	29.62	34.55
14.97	19.96	25.04	52	—	28.78	33.86
14.07	19.09	24.23	53	22.94	27.94	33.08
13.09	18.22	23.45	54	22.02	27.10	32.33
12.08	17.29	22.64	55	21.03	26.21	31.49
11.09	16.38	21.82	56	20.08	25.34	30.73
10.06	15.44	20.98	57	19.04	—	29.90
09.01	14.48	20.11	58	18.05	23.48	29.08
07.99	13.52	19.24	59	16.95	22.55	28.23
06.91	12.56	18.35	60	15.94	21.59	27.35
05.80	11.53	17.41	61	14.86	20.60	26.50
04.65	10.53	16.49	62	13.75	—	25.60
03.58	09.51	15.55	63	12.68	18.64	24.67
02.39	08.47	14.59	64	11.57	17.62	23.75
01.21	07.42	13.60	65	10.44	16.57	22.82
00.11	06.32	12.56	66	09.30	15.51	21.81
15398.92	05.22	11.63	67	08.14	14.45	20.88
97.70	04.12	10.62	68	07.01	13.37	—
96.49	02.97	09.51	69	05.80	12.28	18.86
—	01.82	08.47	70	04.57	11.18	17.82
94.00	00.66	07.42	71	03.36	10.03	16.81
92.74	15399.46	06.32	72	—	08.86	15.76
91.44	98.28	05.22	73	00.88	07.71	14.66
—	97.06	04.12	74	15299.60	06.54	13.60
88.82	95.86	02.97	75	98.31	05.34	12.47
—	94.60	01.82	76	96.98	—	11.36
86.14	93.33	00.66	77	95.72	02.92	10.22
84.77	—	15399.46	78	94.37	01.67	09.07
83.40	90.76	98.28	79	93.04	—	07.91
81.99	89.47	97.06	80	91.64	15299.14	06.79
80.58	88.15	95.86	81	90.28	97.86	05.54
79.15	86.82	94.60	82	88.87	96.55	—
77.68	85.45	93.33	83	87.50	95.22	03.07
76.25	84.09	—	84	86.06	—	01.82
74.75	82.71	90.76	85	84.62	92.52	—
73.25	—	89.41	86	83.17	91.15	15299.31
71.74	—	88.10	87	81.68	89.78	—
—	78.42	86.76	88	80.18	88.40	96.71
68.68	—	85.39	89	78.70	86.98	95.37
67.12	75.47	83.98	90	—	85.54	—
—	73.99	82.55	91	75.59	84.09	—
63.95	72.50	—	92	74.07	82.63	91.29
62.31	70.95	79.72	93	—	81.12	89.90
60.71	69.43	78.20	94	—	79.64	88.48
59.05	67.86	76.83	95	—	78.15	87.06
57.40	—	75.34	96	—	76.64	—
55.70	64.69	73.85	97	—	75.09	84.17
54.02	—	72.29	98	—	73.54	82.71
52.32	—	70.74	99	—	—	81.24
50.58	—	69.23	100	—	—	—
48.86	58.19	67.63	101	—	—	—
47.12	56.54	66.28	102	—	—	—
—	54.84	64.49	103	—	—	—
—	53.14	62.85	104	—	—	—
—	51.42	61.24	105	—	—	—
—	49.69	—	106	—	—	—
—	—	57.94	107	—	—	—

TABLE I. (Continued).

<i>P</i>	(1, 0) band <i>Q</i>	<i>R</i>	<i>J''</i>	<i>P</i>	(1, 1) band <i>Q</i>	<i>R</i>
		15356.22	108			
		54.56	109			
		52.86	110			
			10		15184.77	
			11		84.60	
			12		84.42	
			13		84.17	
			14		83.98	
			15		83.75	
			16		83.51	
			17		83.23	
			18		82.94	
			19		82.71	
			20		82.39	
			21	15180.08	82.07	
			22	79.66	81.75	
			23	79.18	81.42	
			24	78.78	81.02	
			25	78.28	80.69	
			26	77.82	80.33	
			27	77.28	79.88	
			28	76.76	79.48	
			29	76.23	79.01	
			30	75.72	78.58	
			31	75.14	78.10	
			32	74.57	77.61	
			33	73.93	77.12	
			34	73.36	76.61	
			35	72.74	76.07	
			36	—	75.52	
			37	71.45	74.97	
			38	—	74.39	
			39	—	73.79	
			40	—	73.19	
			41	68.63	72.58	
			42	67.89	71.98	
			43	67.16	71.28	
			44	66.35	70.61	
			45	65.63	69.95	
			46	64.86	69.26	
			47	64.05	68.63	
			48	63.23	67.89	
			49	62.40	67.16	
			50	61.54	66.35	
			51	60.73	65.63	
			52	59.84	64.86	
			53	58.96	64.05	
			54	58.05	63.23	
			55	57.14	62.40	
			56	56.20	61.54	
			57	55.27	60.73	
			58	54.30	59.84	
			59	53.32	58.96	
			60	52.32	58.05	
			61	51.30	57.14	
			62	50.30	56.20	
			63	49.27	55.27	
			64	48.20	54.30	
			65	47.13	53.32	
			66	46.07	52.32	
			67	44.97	51.30	
			68	43.86	50.30	
						15182.59
						—
						81.91
						81.53
						81.15
						80.69
						80.33
						79.88
						79.48
						79.01
						78.58
						78.10
						77.61
						77.12
						76.61
						76.07
						75.52
						74.97
						74.39
						73.79
						73.19
						72.58
						71.98
						71.28
						70.61
						69.95
						69.26
						68.63
						67.89
						67.16
						66.35
						65.63
						64.86
						64.05
						63.23
						62.40
						61.54
						60.73
						60.30
						59.84
						58.96
						58.05
						57.14
						56.20
						55.27
						54.30
						53.32
						52.32
						51.30
						50.30
						—
						60.42
						59.54
						58.68
						57.76
						56.82

TABLE I. (Continued).

<i>P</i>	(0, 1) band <i>Q</i>	<i>R</i>	<i>J''</i>	<i>P</i>	(0, 2) band <i>Q</i>	<i>R</i>
—	15239.23	15245.84	69	15142.72	15149.27	15155.87
15231.50	38.16	44.86	70	41.59	48.20	54.92
30.33	37.01	43.84	71	40.43	47.13	53.95
29.12	35.92	42.81	72	39.26	46.07	52.98
27.92	34.80	41.80	73	38.08	44.97	51.96
26.72	—	40.74	74	36.88	43.86	50.94
25.47	—	39.67	75	35.66	42.72	49.89
24.16	31.32	38.57	76	34.44	41.59	48.90
22.89	30.14	37.53	77	33.21	40.43	47.82
21.60	28.94	36.37	78	31.94	39.26	46.73
20.32	27.72	35.26	79	30.67	38.08	45.63
18.95	26.47	—	80	29.40	36.88	44.51
17.65	25.27	—	81	28.10	35.66	43.40
16.26	23.97	—	82	26.76	34.44	42.26
14.92	22.69	30.61	83	25.44	33.21	41.11
13.51	21.41	29.43	84	24.11	31.94	39.91
12.15	20.08	28.17	85	22.73	30.67	38.78
10.72	18.76	26.96	86	21.37	29.40	37.58
09.30	17.45	25.68	87	19.97	28.10	36.35
07.83	16.07	24.40	88	18.56	26.76	35.09
06.39	14.70	23.13	89	17.14	25.44	33.88
04.92	13.33	21.84	90	15.71	24.11	32.65
03.43	11.92	20.55	91	14.25	22.73	31.38
01.94	10.51	19.21	92	12.79	21.37	30.07
00.42	09.08	17.87	93	11.32	19.97	28.75
15198.88	07.64	16.52	94	09.82	18.56	27.45
97.34	06.16	15.15	95	08.30	17.14	26.15
95.78	—	13.74	96	06.79	15.71	24.76
—	03.16	12.33	97	05.25	14.25	23.42
92.53	01.70	10.87	98	03.72	12.79	22.06
91.04	00.20	09.50	99	02.12	11.32	20.66
89.40	15198.61	08.02	100	00.55	09.82	19.24
87.77	97.10	06.59	101	15098.96	08.30	17.84
—	95.53	05.14	102	97.33	06.79	16.41
—	—	03.62	103	—	—	—
—	—	02.08	104	—	—	—
—	90.72	00.56	105	—	—	—
—	89.06	15199.04	106	—	—	—
—	87.44	97.47	107	—	—	—
—	—	95.88	108	—	—	—
—	—	94.32	109	—	—	—
—	—	92.69	110	—	—	—
—	—	91.04	111	—	—	—
—	—	89.40	112	—	—	—
—	—	87.77	113	—	—	—

After the lines of the branches had been sorted out, the $\Delta_2 F'$'s were obtained and used to determine the absolute values of the quantum numbers and the magnitude of the constants B' and B'' according to the equations:

$$\Delta_2 F'(J') = R(J'') - P(J'') = 4B'(J' + \frac{1}{2}) + 8D'(J' + \frac{1}{2})^3 \quad (2)$$

$$\Delta_2 F''(J'') = R(J'' - 1) - P(J'' + 1) = 4B''(J'' + \frac{1}{2}) + 8D''(J'' + \frac{1}{2})^3 \quad (3)$$

The higher power terms, $12F(J + \frac{1}{2})^5$ etc., have been omitted from these equations because calculation shows them to be negligible in the case of potassium. The calculation of the B 's was made by successive approximations and least squares, the D 's being determined by the equations

$$D_v = D_e + \beta(v + \frac{1}{2}) \quad (4)$$

$$D_e = \frac{-4B_e^3}{\omega_e^2} \quad (5)$$

$$\beta = \frac{\alpha^2}{6\omega_e} + \frac{20\alpha B_e^2 - 32x_e B_e^3}{\omega_e^2} \quad (6)$$

The values of ω_e and x_e in Eqs. (5) and (6) were taken from a paper by Crane and Christy⁷ which gives the vibrational constants of the red system of K_2 as follows:

$$\begin{aligned} \nu &= \nu_0 + \omega_e'(v' + \frac{1}{2}) - \omega_e'x_e'(v' + \frac{1}{2})^2 - \omega_e''(v'' + \frac{1}{2}) + \omega_e''x_e''(v'' + \frac{1}{2})^2 \\ &= 15377.73 + 74.73(v' + \frac{1}{2}) - 0.327(v' + \frac{1}{2})^2 - 92.64(v'' + \frac{1}{2}) \\ &\quad + 0.354(v'' + \frac{1}{2})^2 \end{aligned} \quad (7)$$

The constants α' and α'' of the equation

$$B_v = B_e - \alpha(v + \frac{1}{2}) \quad (8)$$

were calculated, after the true J 's had been assigned as just described, but before the final adjustment of the B 's was made, from the variation of the differences of the Q lines of different bands, according to the equations

$$Q(1, 0) - Q(1, 1) = Q_0(1, 0) - Q_0(1, 1) - \alpha''(J + \frac{1}{2})^2 + \beta''(J + \frac{1}{2})^4 \quad (9)$$

$$Q(1, 1) - Q(0, 1) = Q_0(1, 1) - Q_0(1, 0) - \alpha'(J + \frac{1}{2})^2 + \beta'(J + \frac{1}{2})^4 \quad (10)$$

Finally, the combination defects in the (1, 0), (1, 1) and (0, 1) bands were expressed by the theoretical relations

$$\begin{aligned} R(J'') - Q(J'') - Q(J'' + 1) + P(J'' + 1) \\ = (B_{PR}' - B_Q')(J'' + 3/2)^2 + (J'' + \frac{1}{2})^2 \\ \cong 2(B_{PR}' - B_Q')(J + 1)^2 \end{aligned} \quad (11)$$

and the coefficient ($B'_{PR} - B'_Q$) determined by least squares to be 2.02×10^{-6} . This is in adequate agreement with the theoretical expression for this quantity.

$$B_{PR}' - B_Q' = 4B^2/\nu(^1\Pi_u^1\Sigma_u^+) = 2.52 \times 10^{-6} \quad (12)$$

which has been found by Mulliken and Christy⁸ to hold well for the corresponding $^1\Pi$ states of the similar molecules H_2 , Li_2 and Na_2 . The combination

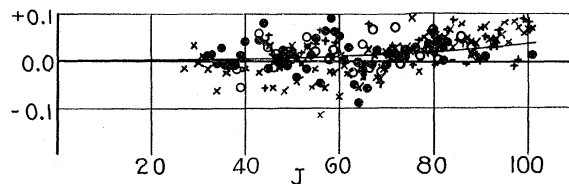


Fig. 1. PQR combination defect. Full circles, hollow circles, \times 's and $+$'s represent data from bands (1, 0), (1, 1), (0, 1) and (0,2) respectively.

defects of Eq. (11) are plotted in Fig. 1. The curve represents the function $4.04 \times 10^{-6}(J+1)^2$.

⁷ Crane and Christy, Phys. Rev. **36**, 421 (1930).

⁸ Mulliken and Christy, Phys. Rev. **38**, 87 (1931).

The rotational constants as above determined are summarized in Table II.

TABLE II. Rotational constants of K_2^{89} molecule.

	Ground state ($^1\Sigma_g^+$)				Upper state ($^4\Pi_u$)		
	equil.	0	1	2	equil.	0	1
B	0.05622	0.05611	0.05589	0.05567	0.04824	0.04812	0.04788
$D \times 10^8$	-8.28	-8.32	-8.41	-8.49	-8.06	-8.09	-8.17
α	0.000219				0.000235		
β	-0.083×10^{-8}				-0.074×10^{-8}		
I_e	492.0×10^{-40}				573.4×10^{-40}		
r_e	3.91×10^{-8}				4.22×10^{-8}		
$B_{PR} - B_Q$					2.0×10^{-6}		

The accuracy with which the values of B and D in Table II represent the $\Delta_2 F'$'s, as well as the precision with which the combination relations hold, is

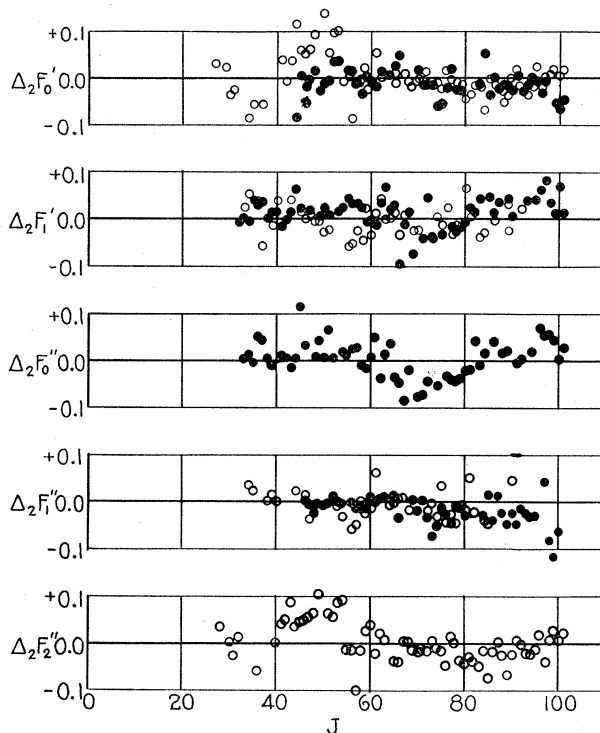


Fig. 2. Residuals of $\Delta_2 F'$'s from those calculated by Eqs. (2) and (3) with constants in Table II. Full circles represent data from bands (0, 1) and (1, 0), hollow circles data from bands (1, 1) and (0, 2).

shown in Fig. 2, wherein the residuals of the observed $\Delta_2 F'$'s from those calculated by Eqs. (2) and (3) are plotted against J . The fact that these representations are within the experimental error of observation (which is far from true of the representations with the quadrupled value of D/B which would have been called for by Eq. (5) had it been assumed that alternate

TABLE III. Comparison of constants of similar molecules^a

	Ground state: $1\Sigma_g^+$		Upper state: $1\Pi_u$		Upper state: $1\Sigma_u^+$	
	H ₂	Li ₂	H ₂	Li ₂	H ₂	Li ₂
F_0	0	0	99086	20398	15369	14022
B_0	59.19	0.6691	29.4	0.5532	0.04812	0.495
$r_e \times 10^8$	0.74	2.67	1.05	2.93	4.22	3.11
α	2.79	0.00744	1.2	0.00804	0.000235	0.005
$-D_0 \times 10^6$	33596	9.952	18051	9.531	0.0809	0.38
ω_e	4371	349.9	2446	270.4	74.73	7.7
$\omega_e x_e$	113.5	2.5	66.5	3.1	0.327	115.6
B_e/ω_e	0.0139	0.00192	0.0123	0.00206	0.000646	0.00196
$R=2x_e B_e/\alpha$	1.13	1.29	1.36	1.59	1.80	1.8
D (volts)	4.34	1.14	2.25	0.46	0.22	1.25
						1.01
						0.38
						0.153
						0.00061
						1.8
						1.9
						0.68
						11672
						(0.042)
						(4.5)
						(0.00010)
						(0.063)
						69.09

^a The data in Table III have been taken from the following sources: for hydrogen, Hyman, Phys. Rev. **36**, 187 (1930) and Birge, Proc. Nat. Acad. **14**, 12 (1928); for lithium, Harvey and Jenkins, Phys. Rev. **35**, 789 (1930), Wurm, Zeits. f. Physik **58**, 562 (1929) and 59, 35 (1929), Loomis and Nusbaum, Phys. Rev. **38**, 147 (1931); for sodium, Loomis, Phys. Rev. **31**, 323 (1928), Loomis and Nile Phys. Rev. **32**, 873 (1928), Loomis and Wood, reference 6; for potassium, Crane and Christy, Phys. Rev. **36**, 421 (1930), and as yet unpublished information from Loomis and Nusbaum as to the heats of dissociation for potassium and sodium.

lines of the bands were missing) is additional definite proof that the latter hypothesis is wrong and that the spin of the K^{39} nucleus is not zero. A further and independent proof of this is that the frequencies of the band lines can be represented by the formulae

$$R, P(J'') = \nu_0 + B' \pm 2B'(J'' + \frac{1}{2}) + (B' - B'')(J'' + \frac{1}{2})^2 \quad (13)$$

$$\pm 4D'(J'' + \frac{1}{2})^3 + (D' - D'')(J'' + \frac{1}{2})^4$$

$$Q(J'') = \nu_0 + (B' - B'')(J'' + \frac{1}{2})^2 + (D' - D'')(J'' + \frac{1}{2})^4 \quad (14)$$

in which the constants are those, given in Table II, which were determined from the $\Delta_2 F'$'s. Had alternate lines been missing the quadratic coefficients in Eqs. (13) and (14), for instance, would have been twice the difference of the B 's determined as above. It has not been thought worthwhile to include graphs showing the agreement between measured and calculated frequencies, but it is within about 0.3 cm^{-1} and systematic deviations could be practically eliminated by adjusting the coefficients, within the limits of error with which they can be determined from the $\Delta_2 F'$'s. The result would not, however, be an increase in the precision of our knowledge of these coefficients, but only of certain differences between them which are not particularly significant, so it has not been done.

In Table III a comparison is made between some of the constants of these two states of the K_2 molecule and those of the corresponding states of the similar molecules H_2 , Li_2 and Na_2 . Data for the upper ($^1\Sigma_u^+$) states have been added for completeness. Since the rotational constants of this state of potassium have not been determined (it would necessitate an analysis of the infrared K_2 system) they have been estimated by extrapolating values for B_e/ω_e and for $R = 2x_e B_e/\alpha$ and by using these to calculate the others. Values based on these extrapolations are given in parentheses. The data in Table III have been compiled from various sources, as indicated in the footnotes. Particularly in the case of hydrogen, difficulties have been encountered owing to contradictions and incompleteness with which the data have been reported, but the data are more than good enough for the purpose of Table III, which is to show the nature of the variations of the various constants along the series of homologous molecules.

The alternation of intensities is most obvious in the 0, 2 band and especially so in the region where for a long interval the lines $Q(M)$ fortuitously coincide closely with $P(M-6)$. It is the lines with odd values of J'' which are stronger, just as has been found to be the case with H_2 , Li_2 and Na_2 .¹⁰ This signifies that the K^{39} nuclei also obey the Fermi-Dirac statistics. The present observations were made under conditions that do not permit the determination of nuclear spin from the ratio of alternating intensities, but it is hoped to make this determination at a later time.

It is probable that lines due to the molecule $K^{39}K^{41}$ would be sufficiently intense to be found if they were sought for, but as no particular interest attaches to them this has not been done. The lines of the molecule $K^{41}K^{41}$, which would be interesting, are probably too faint to be found.

¹⁰ Urey, Phys. Rev. **38**, 1074 (1931).