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The Molecular Spectrum of He^3

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The band spectrum of the molecule $(He^3)_2$ has been studied in the region from 3000A to longer wavelengths. The present paper treats the band system $3p^3\Sigma \rightarrow 2s^3\Sigma$. The rotational and vibrational molecular constants have been determined.

I. INTRODUCTION

IT is well known that excited helium atoms form a diatomic molecule emitting a well-developed band spectrum which lies chiefly in the visible and the neighboring parts of the ultraviolet and infra-red.[1] It formed the subject of a large number of investigations and its structure is fairly well known. Nevertheless it presents still a number of problems which can be studied with improved facilities now that the lighter isotope He^3 is available for spectroscopic studies.

The structure of the band spectrum of helium is in many ways analogous to that of the spectrum of the hydrogen molecule. Its regularities are, however, much more easily unraveled and may thus often serve as a guide for the much more difficult study of the molecular spectrum of hydrogen. This parallelism is much more direct now that the two isobaric molecules, He_2^3 and $H_2^3(T_2)$ may be compared. A study of the band spectrum of He^3 seemed, therefore, highly desirable. Such a study would give as one immediate result a reliable determination of the nuclear spin of He^3.

II. EXPERIMENTAL PROCEDURE

A Pyrex tube of conventional design with aluminum electrodes and a capillary of 8 mm outer diameter was filled at Los Alamos to a pressure of 25 mm with He^3 obtained from the decay of tritium. The tube was intended for end-on observation. It is usually stated that the He_2 spectrum appears best in a wide tube with a mildly condensed discharge when the helium is very pure. We found no difficulty in obtaining it with great intensity in the capillary by excitation with an ordinary neon sign transformer with currents of about 20 to 200 ma. The appearance of the He_2 spectrum in such discharges has been reported previously.[2] It was found that even with a fair amount of impurities the principal He_2 bands appear with considerable strength. In the first tube filled with He^3 we did not succeed in eliminating traces of argon, nitrogen, oxygen, carbon, and hydrogen. In the beginning the bands caused by such molecules as N_2^+, CH, and CO obliterated the He_2 bands completely. After running the tube for some time, however, the impurity gases cleaned up, and, although the atomic lines of the elements mentioned were still much in evidence, the He_2 bands were not interfered with seriously. It turned out that the gas was entirely free from any detectable traces of He^4.

A second tube was prepared with the walls and electrodes more carefully outgassed. The He^3 gas was passed into the tube through a coil immersed in liquid helium. This froze out all impurities, and none showed spectroscopically except small traces of oxygen, hydrogen, and mercury. These did not interfere appreciably with the molecular spectrum of He^3.

Between 3000 and 5000A the spectrum was photo-

* The spectroscopic work was carried out under a contract between the AEC and the Johns Hopkins University.

[1] W. E. Curtis, Proc. Roy. Soc. **A89**, 146 (1913); E. Goldstein, Verh. d. D. Phys. Ges. **15**, 402 (1913). Many other papers particularly between 1922 and 1930.

[2] Y. Fujioka, Zeits. f. Physik **52**, 657 (1928); W. F. Meggers and G. H. Dieke, Bur. Stand. J. Research **9**, 121 (1932).

TABLE I.[a] The $3p^3\Pi \rightarrow 2s^3\Sigma$-system of He_2^3.

K	P branch ν	P branch I	Q branch ν	Q branch I	R branch ν	R branch I	
			0→0 band at 4650A				
0	—	—	—	—	21 518.42	134	
1	—	—	21 498.60	69.1	535.78	64.2	
2	21 458.17	78.0	496.38	318	551.72	289	
3	435.46	42.4	493.08	132	566.26	82.2	
4	411.44	171	488.70	481	579.41	262	
5	386.18	125	483.23	186	591.11	83.8	
6	359.73	214	476.66	465	601.35	229	
7	332.07	72.8	469.06	143	610.16	67.2	
8	303.32	196	460.37	396	617.52	178	
9	273.45	71.4	450.68	106	623.44	51.3	
10	242.52	161	439.91	280	627.91	119	
11	—	—[b]	428.17	71.4	630.95	64	
12	177.70	90	415.38	164	632.58	97	z
13	143.85	28.8	401.63	48.3	632.58	97	z
14	109.14	61	386.98	125	631.50	64	
15	073.64	12.8	371.38	27.2			
16	037.35	32	354.85	56.7	624.85	24.3	
17	000.37	6.1	337.48	14.4	619.56	6.4	
18	20 962.74	21.6	319.22	30.3	612.88	13.0	
19	924.46	3.8	300.11	12.3	604.93	4.1	
20	885.64	7.0	280.20	13.8	595.62	5.6	
21	846.28	2.4	259.56	4.4	585.12		
22	806.58	3.0	238.12		573.33	3.2	
23	766.47	1.9			560.38		
24	726.04	2.3			546.41		

Intensities are quantitative photoelectric measurements at a current of 117 ma through the tube, except P 12 to P 24 which are estimates from microphotometer curve.

				0→1 band near 5122A				
0	—	—		—	—	19 536.47	70	z
1	—	—		19 517.40	60	c	554.63	103	z y
2	19 478.45	44	z	516.83	170	z	572.04	115	x z
3	457.83	26		515.57	70		588.84	46	
4	436.97	180	z	514.15	145		605.41	102	
5	415.28	36		512.36	73	z	620.26	45	
6	393.29	85		510.24	140		634.98	98	
7	370.81	35		507.76	63		648.96	38	
8	347.98	77		505.05	120		662.22	71	
9	324.74	29	(z)	501.97	51		674.76	27	
10	301.22	70		498.66	100		686.69	58	
11	277.56	20	c	495.07	32		697.99	16	
12	253.53	41		491.24	70		708.41	26	
13	229.37	11		487.21	18		718.07	11	x z
14	205.13	24		482.98	44		727.47	21	
15	180.75	6		478.45	44	z	736.04	9	
16	156.54	23		474.00	24		744.05	14	
17				469.39	6		751.43	6	
18				464.66	17		758.36	8	
19				460.03	3		764.42	28	x y
20				455.17	6		770.58	2	x

Intensities are photographic densities multiplied by 100.

				1→0 band near 4274A				
0	—	—		—	—	23 407.89	1	
1	—	—		23 388.07	00		423.87	0	
2	23 347.66	00		384.44	4		437.82	3	
3				379.09	1		449.53	1	
4	297.48	2		371.96	5		459.29	3	
5	269.56			363.04	2				
6	239.54	3		352.38	4		472.29	3	
7	207.74	0		339.86	2		475.69	1	z
8	174.22	3		325.72	4		476.80	3	
9				309.78	2		475.69	1	z
10				292.26	3		472.84	2	
11				272.86	0				
12				251.88	3		460.31	1	
13					4				
14				204.89	1				

Intensities are eye estimates.

TABLE I.—*Continued.*

K	P branch ν	P branch I	Q branch ν	Q branch I	R branch ν	R branch I	
			1→1 band near 4670A				
0	—	—	—	—	21 425.88	7.0q	
1	—	—	21 406.75	3.6q	442.56	4.2q	
2	21 367.83	3.6q	404.66	16.3q	458.17		z
3	345.96	2.7	401.64	z	472.01	5.6q	
4	322.84	9.9	397.33	24.9q	484.65		
5	298.51	3.4	392.07	9.3q	495.81		
6	273.05	12.6	386.08	y	505.77	16.0q	
7	246.50		378.62	9.3q	514.30		
8	218.99	z	370.37		521.41	13.6q	
9	189.91		361.10	7.9	527.11	3.2	
10	160.45		350.92	23.4	531.48	8.1	
11	129.79		339.75	4.3	534.32		y c
12	098.31	5.0	327.67	11.0			c
13	065.96	2.5	314.67	3.2	535.21		c
14	032.79	3.4	300.78	6.5	532.96	15.3	
15	20 998.91	2.1	286.09		529.34	4.0	
16	964.39	2.7	270.50	4.5	524.38	6.5q	
17	929.66		254.13				
18		2.3	236.99		510.18		
19	857.16		218.99	z			
20	820.51		199.99				

Intensities: Those marked q are quantitative photoelectric measurements on the same scale as for the 0→0 band. The rest are estimates from a microphotometer curve.

				1→2 band near 5119A				
0	—	—		—	—	19 547.42		c
1	—	—		19 529.18	3		564.91	4	
2	19 491.88	2		528.59	18		582.06	60	z
3	472.16	2		527.72	6		597.49	5	x
4	452.13		c	526.59	23		613.90	12	
5	431.61	3		525.22	9		628.97	5	
6	410.78	12		523.54	26		643.54	14	
7	389.66	6	c	521.62	10		657.20	6	x
8	368.12	17		519.52	23		670.62	12	
9	546.36	4		(517.20)		c z	683.34	4	
10	324.60	29	z	514.71	20	c	695.34	10	
11	302.53	5		(512.19)	73	z	706.97	3	
12	279.89	8		509.22	18	c	717.90	11	z
13				506.26	3				
14	234.21	5		503.16	8				
15				500.08	5	c			
16				496.98	5				

Intensities same as for 0→1 band.

				2→2 band near 4688A				
0	—	—		—	—	21 344.05	2	
1	—	—						
2	21 288.42	1		21 323.75	3		374.96	4	
3				320.77	1		388.13	8	y
4	245.10	3		316.84	4		400.71	5	
5				311.96	2		409.47	2	
6				306.15	5		421.32	4	
7				299.45	3				
8	145.80	4		291.67	3		436.67	4	
9	118.50	0		283.06	2				
10	090.30	4		(273.50)			446.89	3	
11				263.29	2				
12	031.31	2		251.97	3		451.70	4	

Intensities are eye estimates.

[a] The letters in the column after the intensities have the following meaning: c = line confused with a neighboring one, no reliable intensity measurement possible. x = line diffuse, probably blend. y = line too strong for the classification, probably blend. z = line coincides with another classified line.

[b] Covered by the atomic line 4713A.

graphed in the second order of a 21-ft. grating Paschen spectrograph with a dispersion of about 0.6A/mm, between 5000 and 9000A in the first order of the same spectrograph (dispersion 1.2A/mm) and beyond 9000A in the first order of a 21-ft. Wadsworth mounting (dispersion 5.01A/mm). The exposure times ranged from 20 min. for the stronger bands to 48 hr. for the weaker ones. A general continuous background particularly in the region below 5000A sets the limit for the weakest lines that can be observed. Possibly the background is due, at least partly, to traces of impurities left in the tube. An attempt will be made to remedy this with an even more carefully purified tube. Weak molecular lines in the vicinity of the greatly overexposed atomic helium lines are obscured by the irradiation and ghosts from the atomic lines.

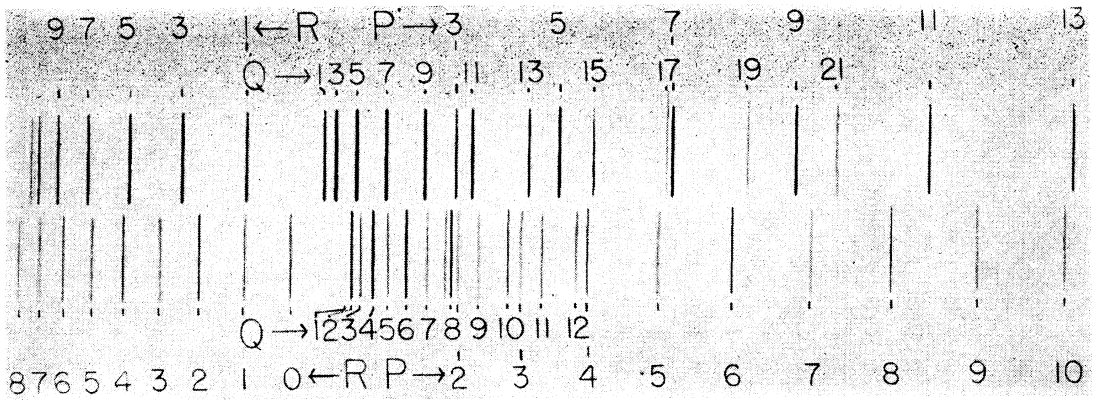

FIG. 1. The 4650 bands of He_2^4 (above) and He_2^3 (below).

The dispersion obtained for the He_2^3 bands is in general considerably better than that with which the analogous He_2^4 data in the literature[3] were obtained. Accordingly the constants for He_2^3 can be regarded as more accurate than the accepted He_2^4 constants. An increase in resolving power and dispersion is, of course, always desirable because of the higher accuracy that can be achieved. For He_2^3 this is essential in the denser parts of the spectrum because the average spacing of the lines is only two-thirds that of the He_2^4 lines.

III. RESULTS

The present paper contains one of the principal band systems, $3p^3\Sigma \rightarrow 2s^3\Sigma$, the 0→0 band of which near 4650 is possibly the strongest band in the spectrum. The analogous data for He_2^4 were given by Curtis[4] (0→0 band), Weizel and Füchtbauer[5] (0→1, 1→1 bands), and Dieke, Takamine, and Suga[6] (1→0, 1→2, 2→2 bands). Table I gives the wave numbers and intensities of the six bands comprising the system. These are exactly the same bands that are also known for He_2^4. There may be additional weak bands of this system hidden among the stronger lines which may be found when the spectrum is more completely classified.

TABLE II. The $3p^3\Pi \rightarrow 2s^3\Sigma$-system of He_2^4.

K	P branch ν	P branch I	Q branch ν	Q branch I	R branch ν	R branch I
			0→0 band near 4648A			
1	——		21 506.42	298	21 534.68	280
3	21 458.88	182	502.28	552	558.08	360
5	421.92	319	494.80	716	577.41	389
7	381.39	314	484.06	632	592.67	319
9	337.41	282	470.11	536	603.74	237
11	290.18	222	452.99	382	610.66	160
13	239.91	164	430.13	238	613.50	40
15	186.79		409.57	143	612.19	
17			383.98	84	606.94	
19					597.71	

The intensities are photoelectric measurements at a current of 84.5 ma (d.c.) through the tube.

Table II gives the 0→0 band of He_2^4 obtained under the same circumstances as the He_2^3 bands. We believe that these data are considerably more accurate than the original measurements of Curtis.[4]

The intensities listed in Table I and II are partly photoelectrically measured values obtained at a current of 110 ma through the discharge tube. These values should be quite accurate. The other intensities are estimates from microphotometer traces. No attempts were made to obtain a completely consistent intensity scale for the weaker lines. More data on the intensities will be given in a subsequent paper (see also Section V of the present paper). As a general guide it may be stated that under the conditions under which we worked the strong molecular lines are about 1000 times weaker than the strong atomic lines and that the 1→1 band is about 19 times weaker than the 0→0 band.

Figure 1 gives a reproduction of the 0→0 band taken in the second order of a 21-ft. Wadsworth mounting together with the 0→0 band of He_2^4. It shows that the qualitative differences between the two bands are as they must be expected. (1) The origin of the He_2^3 band (in the vicinity of the Q_1 line) is displaced to longer wave-lengths because of the increased zero-point vibrational energy. (2) In He_2^4 the even-numbered rotational lines are absent because of the zero nuclear spin of He^4. These lines are present in He_2^3 and actually stronger than the odd-numbered lines. This is in accordance with the fact that He^3 possesses a nuclear spin and because it has an odd number of nucleons, and, therefore, different statistics from that of He^4. (3) The spacing of the rotational lines is wider in He_2^3 because of the smaller moment of inertia.

[3] In the original work of Curtis (reference 4) only the 4650 band was obtained in the third order of a 10-ft. grating spectrograph with a dispersion of 1.7A/mm, the rest with 2.5 and 5.0A/mm, respectively. The maximum dispersion achieved for the stronger bands in the later work was 1.4A/mm [Dieke, Takamine, and Suga, (reference 6)].

[4] W. E. Curtis, Proc. Roy. Soc. **A103**, 315 (1923).

[5] W. Weizel and C. Füchtbauer, Zeits. f. Physik **44**, 431 (1927).

[6] Dieke, Takamine, and Suga, Zeits. f. Physik **49** 637 (1928).

TABLE III.

	He_2^3		He_2^4	
	$2s^3\Sigma$	$3p^3\Pi^-$	$2s^3\Sigma$	$3p^3\Pi^-$
B_0	10.046	9.495	7.587	7.170
B_1	9.678	9.151	7.351	6.889
B_2	9.289	8.798	7.096	
D_0	0.000976	0.000908	0.000547	0.000505
D_1	0.000974	0.000916	0.000567	0.000435
D_2	0.000938	0.000855	0.000552	
ω_0	1 981.99	1 890.08	1 732.8	1 652.5
ω_1	1 878.33	1 797.21	1 654.4	1 580.4
(B_e) Y_{01}	10.222	9.664	7.698	
α Y_{11}	−0.3465	−0.3346	−0.217	
Y_{21}	−0.0106	−0.0047	−0.0095	
Y_{10}	2 085.65	1 982.95	1 811.2	1 724.6
Y_{20}	51.83	46.44	39.2	36.0
ν_e	21 549.79		21 549.54	

IV. MOLECULAR CONSTANTS

The constants occurring in the rotational and vibrational energies are listed in Table III. The constants are those occurring in the expression for the vibrational and rotational energy

$$E(K, V)=\Sigma Y_{m,n}K^n(K+1)^n(V+\tfrac{1}{2})^m, \qquad (1)$$

and the usual abbreviations are used for

$$B_v=\Sigma_m Y_{m,1}(V+\tfrac{1}{2})^m, \quad D_v=\Sigma_m Y_{m,2}(V+\tfrac{1}{2})^m.$$

The rotational constants were obtained in the usual way with a least-square method from the first eight rotational differences for $2s^3\Sigma$ for which (1) can be regarded as a good enough approximation with only two terms ($n=1, 2$). The constants for $3p^3\Pi^-$ were obtained from the first eight lines of the Q branches. It is known that the rotational constants for the $3p^3\Pi^+$-levels which give rise to the P and R branches have a less simple theoretical interpretation. The band origins of He_2^3 and He_2^4 are given in Table IV.

In the calculation of the constants, care was taken that in the weaker bands lines that obviously were blends (marked z in Table I) were not used. When the frequencies of the lines or differences were recalculated with the constants so obtained, the agreement between calculated and observed values was within the limits of experimental errors in all cases. For the 0⟶0 band the maximum deviation was 0.02 cm^{-1}. For the weaker,

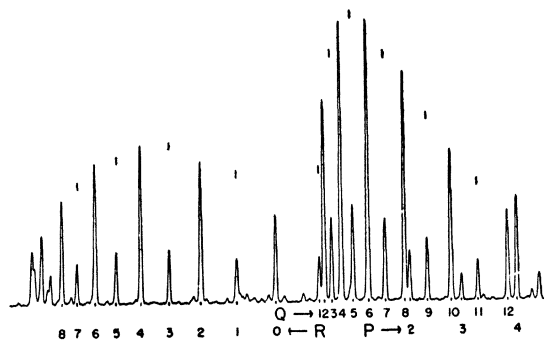

FIG. 2. Photoelectric intensity traces of the 4650 band of He_2^3. The tops of the short vertical lines indicate the intensity of the weak rotational lines multiplied by 3.

TABLE IV. Band origins.

$V'/\pm V''$	0	1	2
	He_2^3		
0	21 499.69	19 517.76	
1	23 389.83	21 407.78	19 529.45
2			21 326.66
	He_2^4		
0	21 502.26	19 773.97	
1	23 159.22	21 427.09	19 772.34
2			21 352.78

bands where interference with other lines has a more serious effect, the deviations are slightly larger.

The constants of He_2^3 and He_2^4 in Table III have the numerical relations expected from the theory of band spectra of isotopic molecules. A precise comparison is not useful at this point because of the less accurate values for He_2^4 which moreover often were calculated by different methods.

V. NUCLEAR SPIN

While the work on this paper was under way a note by Douglas and Herzberg[7] appeared in which the nuclear spin of He^3 was determined as $\frac{1}{2}\hbar$. The results of this section are, therefore, a confirmation of their work. As our results were obtained from different bands by a different method they may be of interest even though the nuclear spin is already known.

The rotational lines in the band of a homonuclear diatomic molecule are alternately strong and weak. The intensities of the strong lines lie on one continuous curve, the weak ones on another one and, if I is the nuclear spin (expressed in units of $\hbar$), the ratio of the ordinates of the two curves is $(I+1)/I$. This ratio is 3:1, 2:1, 5:3, ⋯ if the nuclear spin is $\frac{1}{2}$, 1, $\frac{3}{2}$, ⋯ respectively.

Figure 2 shows a trace of the 4650A band obtained by scanning the spectrum with an electron multiplier photo-tube. The spectrograph used for this purpose was a plane grating monochromator with two off-axis parabolic mirrors of two meters focal length. Entrance and exit slits are fixed and the wave-lengths are changed by rotating the grating. The amplitudes of the traces in Fig. 2 are strictly proportional to the intensities.

The tops of the short vertical lines indicate the amplitudes of the alternate weaker band lines multiplied by a factor of three. It is evident that they lie now on a continuous curve with the strong lines which indicates that the intensity ratio is 3:1 which is characteristic for a nuclear spin $\frac{1}{2}$. It is quite evident that any of the other possible ratios (2:1, 5:3, etc.) would not have brought the two curves to coincidence.

Figure 3 shows a different representation of these data which allows a better quantitative evaluation. As the intensity of a line is

$$I_{n,m}=A_{nm}N_n,$$

[7] A. E. Douglas and G. Herzberg, Phys. Rev. **76**, 1529 (1949).

where A_{nm} is the transition probability (which contains also the factor ν^4) and N_n the number of molecules in the upper state. From this

$$\ln(I_{nm}/A_{n,m}) = \ln N_n = \text{const} - E_n/kT$$

if there is statistical equilibrium and therefore

$$N_n = N_0 e^{-E_n/kT}.$$

The $I_{n,m}$ values are measured, the $A_{n,m}$ for a $\Pi \rightarrow \Sigma$-transition are known. If, therefore, $\ln(I/A)$ is plotted against the empirically known E_n a straight line should result with slope $-1/kT$ and furthermore the points for all lines of a band, whether they be P, Q, or R lines should lie on this one straight line.

Figure 3 shows such a plot for the Q lines of the $0 \rightarrow 0$ band. The weak lines, however, were first multiplied by a factor of three. The fact that they lie then on the same curve as the strong lines shows again that the nuclear spin of He^3 is $\frac{1}{2}$.

The P and R lines have not been entered in order not to confuse the picture. They fall, however, on the same curve as the Q lines, within the limits of experimental errors.

Intensities in the corresponding He_2^4 band were published by Childs.[8] He called attention to several discrepancies between his measurements and the theory, in particular that the points for the three branches did not lie on the same curve. A part of these discrepancies arose from the fact that the proper interpretation of the structure of the bands was not known, but some remain even if Childs' data are treated according to modern views. We believe that the difficulty of obtaining reliable intensities with the photographic method of intensity measurements was responsible for this. All these difficulties disappear if the intensities are obtained photoelectrically. This was confirmed in our laboratory by Mr. Riesz, who made the corresponding measurements for the He_2^4 band.

From this one can conclude that the transition probabilities obtained from the simple theory represent the results adequately.

[8] W. H. J. Childs, Proc. Roy. Soc. **A118**, 296 (1928).

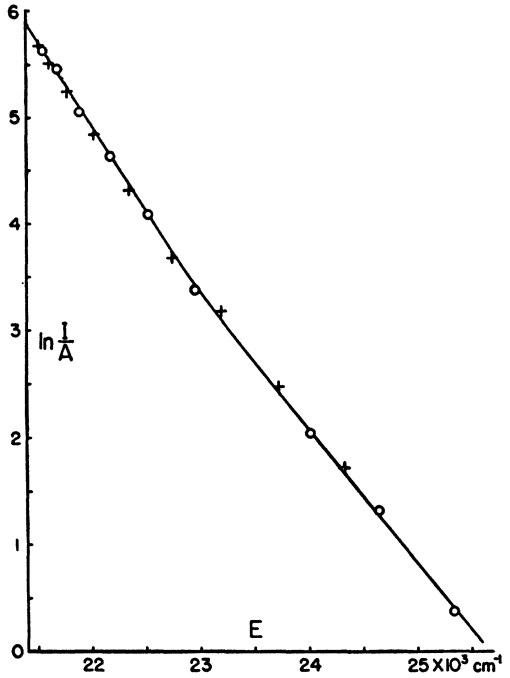

FIG. 3. $\text{Ln}I_{nm}/A_{nm}$ against E_n plot of the intensities in the Q branch of the 4650 band. Circles represent the strong lines, crosses the weak ones multiplied by 3.

Figure 3 shows that there is a slight curvature to the line representing the intensity points. This curvature is different for different currents and may represent a real deviation from thermal equilibrium. Additional measurements which are being undertaken now probably will clear up this point.

The temperatures obtained from the $\ln I/A$ plot range from 580 to 820°K for currents from 20 to 115 ma through the tube. The temperatures obtained in He^4 in a tube of similar construction under equivalent conditions also are of this order of magnitude.

The authors are glad to acknowledge the aid of Mr. F. T. Byrne who photographed the spectrum and made the intensity measurements and of Mrs. Dorothy McVay who made the wave-length measurements.

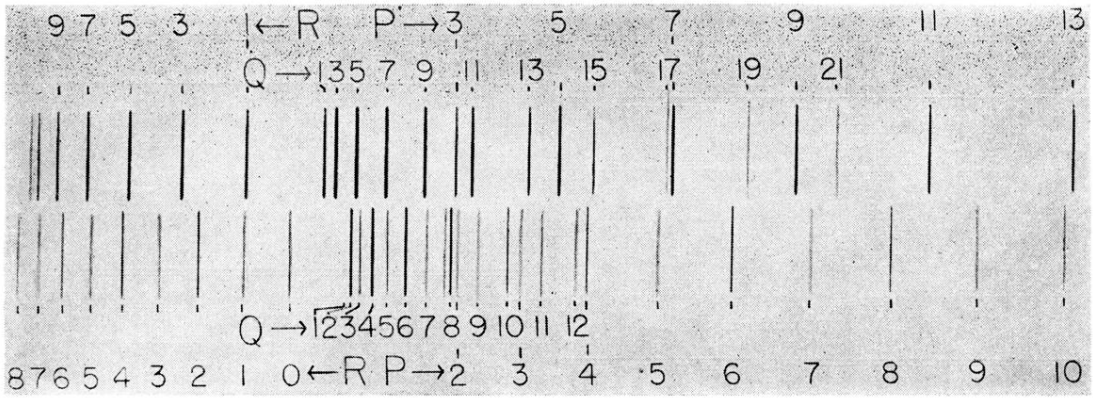

FIG. 1. The 4650 bands of He_2^4 (above) and He_2^3 (below).