The Band Spectrum of Caesium

F. W. Loomis and P. Kusch, *University of Illinois*

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Measurements of five distinct band systems of Cs_2 have been made, in absorption with high and low dispersion, in magnetic rotation, and in fluorescence. Three of these systems, with maxima at 6250A, 7200A, and 7667A, have been reported before, but not analyzed. The fourth with a maximum at 4800A and the fifth, extending from 8950A to limit of sensitivity of the plate, are new. Quantum numbers have been assigned to some 218 bands in the system at 7667A. The upper and lower vibrational frequencies are 34.28 and 41.99 cm^{-1}, and an extrapolation yields 0.45 volt as the energy of dissociation of the ground state. This system, and the one beyond 8950A, apparently correspond to the green and red systems of sodium, respectively. The origin of the fifth system lies beyond the region of sensitivity of even the new Eastman Q plates. Some regularities in the other systems have been found, but no complete analysis could be made, though a fluorescence spectrum was obtained in the 6250 system which showed the lower state to be the same as in the 7667A system. This 6250A system is extraordinarily complex and appears to contain some bands degraded to the red, some to the blue and some narrow regions of absorption bounded by edges on both sides. No magnetic rotation spectrum was found.

THIS investigation was undertaken in order to extend our knowledge of the spectra and heats of dissociation of the alkali metal molecules. Rather complete information is already available[1, 2, 3] with regard to Li_2, Na_2 and K_2, but, although some of the spectra of Rb_2 and Cs_2 have been reported,[4, 5] no satisfactory analysis has been made, nor are any trustworthy values of their heats of dissociation available. Moreover it is to be expected that the heavy elements, in which the atomic spectra show strong spin-orbit interactions, will show in their band spectra an approach to a new type of coupling, at least in the neighborhood of dissociation.

Because caesium is so expensive, it is not feasible to use quite the same apparatus and methods as have been employed with Li_2, Na_2 and K_2. Fortunately, however, its vapor pressure becomes high enough to give well-developed molecular absorption spectra at temperatures so low that glass is only very slowly attacked. The work was therefore done with caesium which was prepared by heating dry caesium chloride with metallic calcium and then distilled, in several stages, *in vacuo*, into the glass absorption tube. In use, the absorption tube was heated to temperatures between 180° and 350°C by means of a coil of wire wound around its whole length and with a little closer winding near the ends to keep the windows hotter than the rest and therefore free from condensed caesium. The absorption spectra were photographed with instruments of various dispersions, including the first order of a 21 foot 30,000 line/inch concave grating in a Paschen mounting, which gave a dispersion of 1.3A/mm. This proved necessary to effect satisfactory resolution of the *vibration* structure in many regions; in no region was it adequate to resolve the rotational structure.

The spectra were also photographed when the caesium was in the presence of 40 cm of argon. The effect of argon was in all regions to cause the bands to appear at lower temperatures. No selective effect was noticed, not even a difference between diffuse bands and those with structure.

An attempt was made to find a magnetic rotation spectrum of Cs_2, to aid in the analysis. The glass absorption tube was put into the solenoid used by Loomis and Nusbaum[1] and long exposures taken in all regions of the visible and photographic infrared spectrum, without success. It cannot be concluded, however, that Cs_2 does not possess any magnetic rotation spectrum, for it may well be that there is one in the infrared, as is to be expected by analogy with Li_2, Na_2 and K_2, but that it cannot be photographed in a reasonable time with the plates available in that region.

Attempts were also made to find fluorescence spectra. Unfortunately there is a dearth of strong lines, suitable for excitation, in the regions

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[1, 2, 3] Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931); **39**, 89 (1932); **40**, 380 (1932).

[4] Walter and Barratt, Proc. Roy. Soc. **A119**, 257 (1928).

[5] Rompe, Zeits. f. Physik **74**, 175 (1932).

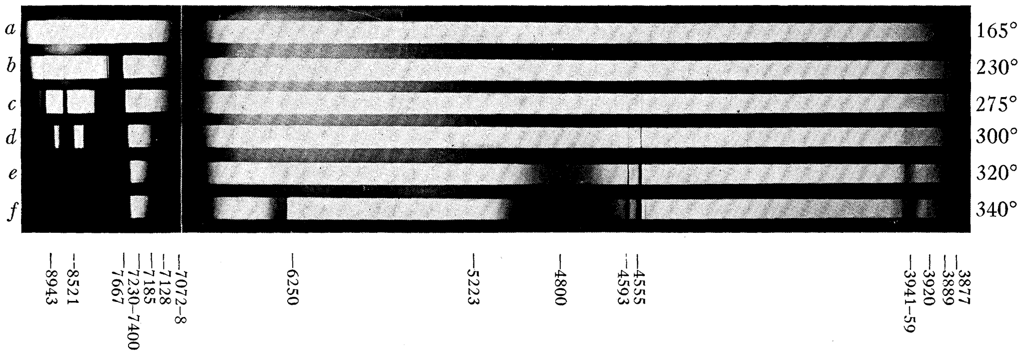

FIG. 1A.

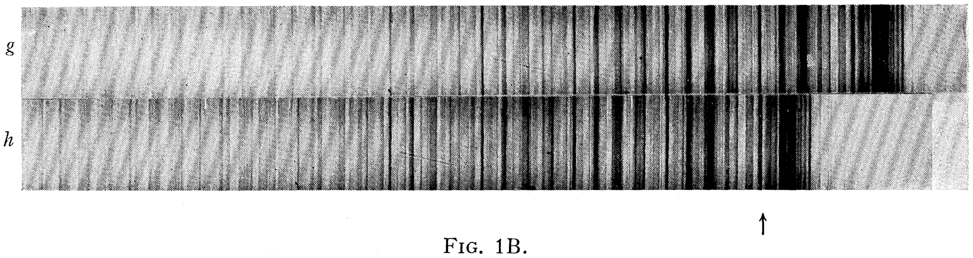

FIG. 1B.

FIG. 1. The band spectra of Cs_2. The spectrograms on the left, *a–f*, were taken on an Eastman 3P plate; those to the right on an Eastman hypersensitive panchromatic plate.

of the caesium absorption bands. Excitation by hydrogen, helium and mercury yielded no results, but a long U-shaped neon tube placed parallel to a caesium tube, and used with Wood's light-furnace[6] technique, yielded a series of fluorescence lines excited by Ne 6402A and with a spacing of 40 cm^{-1}. This demonstrated, what would not otherwise have been evident, that the absorption system at 6250A has a lower state with a vibrational interval 40 cm^{-1} and which is presumably the ground state and identical with the lower state of the 7667A system.

All the band spectra of Cs_2 which have been found in the region 3880–10,500A are shown in Fig. 1, *a–f* which was taken, for this purpose, with a Hilger E63 spectrograph at the temperatures indicated. The following distinct features are apparent:

I. At the extreme right is the 3877, 3889A, $8^2P \leftarrow 6^2S$ doublet of the principal series, in which, at high temperatures, the structure reported by Kuhn[7] and explained by him in terms of polarization molecules, becomes apparent.

II. At 3920A is a single faint sharp band, degraded to the blue, appearing at 300°C, previously reported by Kuhn.

III. A band which Kuhn has reported as a diffuse maximum with a long wave-length edge at 3961A appears at 270°C and at higher temperatures can be clearly seen on our original plates to contain four heads, degraded to short wave-lengths, at 3941, 3947, 3953 and 3959A and to be accompanied, on the long wave-length side by faint diffuse maxima at approximately 3983, 4006, 4035 and 4065A. It was not certain that these diffuse maxima belong to the caesium band systems. They may be part of a band system due to NaCs reported by Walter and Barratt[4] which lies between 3931 and 4315A, and which faintly appears on our plates.

IV. In the neighborhood of the 4555, 4593A, $7^2P \leftarrow 6^2S$ doublet of the principal series appears the structure reported by Kuhn and attributed to polarization molecules.

V. At about 300°C a band system begins to develop in the blue-green, having its maximum intensity at about 4800A. With increasing temperature this system spreads out in both directions. On the short wave-length side, it

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[6] Wood, Phil. Mag. [6] **35**, 235 (1918).

[7] Kuhn, Zeits. f. Physik **76**, 782 (1932).

approaches, and perhaps finally crosses, the 4555, 4593A doublet. On the long wave-length side it terminates rather abruptly at high temperatures in an edge at 5223A, not visible in Fig. 1, which appears very similar to the infrared edge reported and explained by Loomis and Nile[8] in the red system of Na_2 and to other red edges which have since been found in corresponding systems. From these general features, which are very much like those of the $^1\Sigma\leftarrow{}^1\Sigma$ systems of Li_2, Na_2 and K_2 it appears very likely that this is a $^1\Sigma\leftarrow{}^1\Sigma$ system associated with the second doublet of the principal series of caesium. The only previous mention of this system which we have found is by Walter and Barratt[4] who call it a diffuse band with an edge, on the red end, at 5224A. We believe there can be no doubt that it actually belongs to Cs_2, since the faintness of the lines of the other alkali atoms shows that they cannot be present in important amounts, and since this band system does not coincide with any of those attributed by Walter and Barratt[4] to mixed alkali molecules. This system does not, on superficial inspection, appear in any way unusual, but we have not succeeded in making a satisfactory analysis of it. The heads near the center of the system are rather diffuse. In the region of somewhat longer wave-lengths some regularities are apparent and we have been able to assign vibrational quantum numbers to a number of bands, except for unknown additive constants in both v' and v''. The frequencies of these bands, together with those we have been unable to assign, are given in Table I. The numbers n' and n'' are, except for additive constants, equal to v' and v''. The upper vibrational interval is 31 cm^{-1} and the lower is 40 cm^{-1} which latter approximately agrees with that for the ground state of the 7667A system.

VI. At about 360° a very faint system, not previously reported, begins to appear near 5600A. It is too faint to be seen in Fig. 1, but is developed fairly well by the admixture of 40 cm of argon. As the temperature of the caesium-argon mixture is raised the system extends only slightly towards the blue but broadens considerably toward the red and eventually overlaps the system at 6250A. Under low dispersion, in argon, the system appears almost completely diffuse; but in a grating photograph, taken through caesium in vacuo, it is seen to consist of a hopeless confusion of very fine and incompletely resolved lines, with no apparent heads or regularities of any kind.

TABLE I. *Band heads in the system at 4800A.*

ν observed	n''	n'	ν observed	n''	n'	ν observed	n''	n'
21368.8			20971.2			20228.7		
21344.1			20960.2			20268.0	5	0
21315.1			20928.6			20228.2	6	0
21305.4			20827.2			20187.7	7	0
21287.6			20800.1			20164.5		
21276.9			20758.4			20148.3	8	0
21253.2			20704.5			20122.9		
21234.1			20562.3			20108.2	9	0
21221.4			20500.2	0	1	20067.8	10	0
21196.9			20491.1	1	2	20021.7		
21168.7			20461.1	1	1	19982.5		
21139.5			20450.7	2	2	19935.0		
21112.9			20420.1	2	1	19887.1		
21082.1			20410.1	3	2	19851.0		
21056.0			20389.2	2	0	19807.1		
21030.9			20379.4	3	1	19739.3		
21002.9			20339.1	4	1	19696.4		
20988.6			20308.0	4	0	19658.3		

VII. At about 230°C a prominent, but very complex, band system appears near 6250A. Under low dispersion it appears to terminate fairly sharply on the short wave-length side, and to degrade toward long wave-lengths. With higher temperatures it has been followed as far as 6550A. This system has been reported by Rompe.[5] It appears in Fig. 1, *g* and *h*, which are from grating photographs. The bands show no sign of rotational structure, even under the highest dispersion. They vary widely in appearance. Some degrade to the red, some to the blue; some appear as almost sharp lines and some as narrow bands with heads on both sides. Some 258 of them have been measured. We have by no means attained a complete analysis or understanding of this system, or systems, but some regularities have been uncovered.

First, the 6402A line of neon excites a fluorescence series of lines whose frequencies and frequency intervals are given in Table II. It follows that the lower state of this system has a vibrational interval of about 40 cm^{-1}, and this agrees with the ground interval of the system at

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[8] Loomis and Nile, Phys. Rev. **32**, 873 (1928).

TABLE II. *Fluorescence series excited by the 6402A line of neon.*

ν observed	$\Delta\nu$ observed
Ne 15615.2	
	39.9
15575.3	
	41.6
15533.7	
	39.7
15494.0	
	38.7
15455.3	
	38.6
15416.7	

7667A. With this as a basis, the heads of 31 bands, all degraded to the blue, have been assigned to a square array. Their frequencies can be expressed by the formula

$$\nu = 16{,}045.06 + 29.38(n'+\tfrac{1}{2}) - 0.0796(n'+\tfrac{1}{2})^2$$
$$-[41.990(v''+\tfrac{1}{2}) - 0.080051(v''+\tfrac{1}{2})^2$$
$$-0.000164266(v''+\tfrac{1}{2})^3], \quad (1)$$

in which the lower vibration interval agrees with that of the 7667A system. Since the system could not be traced to the origin, n' presumably differs from the true v' by some unknown constant. The observed frequencies, the intensities, quantum numbers and the differences between the measured values and those calculated from Eq. (1) are given in Table III. It is rather surprising however that bands with these upper and lower intervals should be degraded to the blue.

Second, it is clear that there is an important set of intervals beginning with 54.0 cm^{-1} and converging toward the red at the rate of about 0.6 cm^{-1} per quantum number. This can be seen in Fig. 1, *g* and *h*, which are two prints of the same grating photograph, displaced by an amount which, at the points indicated by the arrow, corresponds to 54 cm^{-1}. It will be seen that the spectral regions which are thus brought into conjunction are almost, but not quite, entirely alike, even to the finer details.

Third, there is a set of intervals, starting from about 14 cm^{-1} and converging toward the red, which has been reported by Rompe, and is quite apparent on our plates, but which we are inclined to consider as sequence intervals.

TABLE III. *Band heads in the system at 6250A.*

ν observed	I	v''	n'	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	ν observed	I	v''	n'	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
15770.37	7	7	0	0.02	15594.25	4	15	5	0.04
15758.96	6	8	1	0.07	15587.08	4	13	2	−0.03
15747.38	3	9	2	−0.06	15583.43	4	16	6	0.10
15729.77	5	8	0	0.10	15576.17	4	14	3	−0.19
15695.78	5	11	3	−0.05	15572.57	4	17	7	0.10
15684.60	3	12	4	0.01	15561.41	4	18	8	−0.23
15678.08	4	10	1	0.04	15554.92	4	16	5	0.01
15666.86	5	11	2	−0.07	15544.37	6	17	6	0.17
15655.79	4	12	3	−0.05	15533.70	6	18	7	0.17
15644.74	4	13	4	−0.02	15522.87	6	19	8	0.01
15633.75	4	14	5	0.06	15515.88	5	17	5	0.10
15626.93	4	12	2	−0.01	15505.41	4	18	6	0.15
15622.76	4	15	6	0.13	15495.10	3	19	7	0.35
15611.75	5	16	7	0.15	15484.22	3	20	8	−0.05
15605.06	5	14	4	−0.05	15445.77	5	21	9	−0.09
15600.38	3	17	8	−0.20					

VIII. At 7072, 7075 and 7078A there are three sharp edges, degraded to the blue, which appear as a single diffuse band in Fig. 1 and were so reported by Rompe. The frequencies of their heads, with the intervals between them in parentheses, are: 14,136.79 (6.41) 14,140.38 (6.55) 14,123.83 cm^{-1}. There are also two bands which may really be diffuse, at 7128 and 7185A.

IX. In the region 7230 to 7400A there occurs at 300°C a faint system of ten sharp and accurately measurable bands, degraded to the red. Their frequencies can be expressed by the formula

$$\nu = 13{,}741.74 + 38.46n' - 49.41n'' \quad (2)$$

but since no convergence is apparent in either level, and since neither vibrational interval is the same as any other known interval, the numbers n' and n'' cannot be definitely identified with quantum numbers, nor can certain alternative arrangements, whose spacings are simple linear functions of the above, be excluded. However, the assignment according to Eq. (2) arranges the bands into a more plausible square array than any other. The system extends in both directions until it is overlapped by other structures which make it impossible to follow it further. The measured frequencies of the bands, together with the differences between the observed frequencies and those calculated from Eq. (2) are given in Table IV.

X. The strongest system of the entire spectrum, with its origin at 7667A, appears at about 170°C and with increasing temperature extends in both directions, moving rather slowly toward the blue and rapidly toward the red. The bands are sharp, and accurately measurable on the

TABLE IV. *Band heads in the system at 7200A.*

ν observed	n''	n'	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	ν observed	n''	n'	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
13818.29	0	2	−0.37	13681.37	2	1	−0.01
13780.25	0	1	0.05	13642.86	2	0	−0.06
13758.80	2	3	0.50	13593.00	3	0	−0.51
13730.81	1	1	0.02	13544.04	4	0	−0.06
13692.50	1	0	0.17	13494.90	5	0	0.21

grating plates, and are degraded to the red. It is possible to see that they have rotational structure but it is not sufficiently resolved to be measured. We have measured 343 band heads in this system and have assigned vibrational quantum numbers to 211 of them, including 7 bands for which two alternative assignments are possible. Most of the unidentified bands lie at the red end of the system where it crosses the diffuse bands (XI); a few of them lie near the blue end where there is much overlapping. Near the origin of the system all bands are assigned.

The frequencies of all assigned bands can be represented with satisfactory accuracy by the equation

$$\begin{aligned}\nu = 13{,}043.87 &+ 34.230(v'+\tfrac{1}{2}) \\ &-0.077986(v'+\tfrac{1}{2})^2 - 0.000188149(v'+\tfrac{1}{2})^3 \\ &-[41.990(v''+\tfrac{1}{2}) - 0.080051(v''+\tfrac{1}{2})^2 \\ &\qquad -0.000164266(v''+\tfrac{1}{2})^3]. \end{aligned} \tag{3}$$

The quantum numbers, the measured frequencies, and the differences between the measured frequencies and those calculated from Eq. (3) are given in Table V. The unidentified bands are also included, and in the case of many such bands near the red end of the system their arrangement into apparent sequences is indicated, the sequences being designated by roman numerals and the ordinal numbers of the band heads by arabic ones. Unfortunately, it has not been found possible to fit these sequences, unambiguously, into the quantum number scheme.

The upper and lower vibrational terms of all assigned band heads are plotted in Fig. 2, which is an improved[1] Franck-Condon diagram for the 7667A system. It will be noted that this diagram for this system is a little unusual in that the right arm of the locus is much more extensive, and even extends to higher values of v', than the left arm. This is because the left arm curves to the right so much that the weaker bands, with high v's overlap the stronger ones and cannot be distinguished. Another contributing factor is that the transition probabilities on the left arm are much smaller than on the right arm. This has been found to be the case with the other alkali molecules, notably in Wood's fluorescence experiments with Na_2, and is to be expected theoretically since the left arm corre-

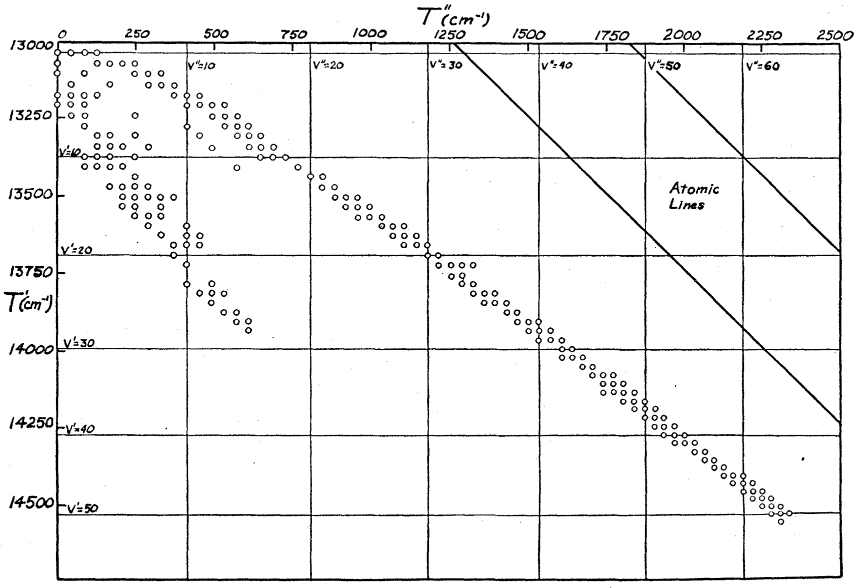

FIG. 2. Improved Franck-Condon diagram for the 7667A system of caesium.

TABLE V. *Band heads in the system at 7667A.*

ν observed	v''	v'	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
13372.42	10	23	0.34
13362.56	11	24	0.44
13352.55	12	25	0.40
13342.30	13	26	0.14
13332.99	14	27	0.82
13328.87			
13327.55	5	15	0.27
13325.36			
13323.71	2	11	0.69
13322.58	12	24	0.46
13322.58	15	28	0.42
13321.23	9	20	0.55
13318.47	6	16	0.55
13311.07	10	21	−0.03
13308.33	7	17	−0.22
13305.02	4	13	0.36
13302.32	14	26	−0.19
13299.43	8	18	0.29
13298.80			
13298.24			
13297.70			
13297.22			
13295.86	5	14	0.39
13294.35			
13292.32	12	23	0.41
13292.32	15	27	−0.37
13291.53			
13290.81	2	10	0.29
13290.19	9	19	0.45
13288.40			
13287.15			
13286.80	6	15	0.52
13284.45			
13283.61			
13282.60	13	24	0.31
13281.98	3	11	0.47
13277.30	7	16	0.24
13263.61	5	13	0.13
13254.63	6	14	0.17
13249.15	3	10	0.14
13249.15	10	19	−0.25
13240.45	4	11	0.28
13236.66	8	16	0.28
13222.84	6	13	0.37
13221.01			
13219.13	10	18	0.84
13216.82	3	9	0.47
13213.68	7	14	0.07
13209.52	0	5	0.47
13209.52	11	19	0.29
13208.11	4	10	0.44
13205.07	8	15	0.33
13203.89			
13200.84	1	6	0.30
13199.33	5	11	0.34
13193.51			
13192.18	2	7	0.15
13190.51	6	12	0.20
13187.36	10	17	0.36
13183.91	3	8	0.39
13181.75	7	13	0.13
13180.07			
13178.31	11	18	0.19
13176.97			
13175.43	0	4	−0.13
13175.43	4	9	0.42
13173.03	8	14	0.10
13167.26	1	5	0.04
13163.26			
13161.11			
13159.02	2	6	0.15
13142.66	4	8	0.48
13133.88	1	4	0.15
13133.88	5	9	0.05
13131.70	9	14	−0.72
13125.79	2	5	0.24
13125.79	6	10	0.31
13108.17	0	2	0.07
13100.12	1	3	0.04
13091.95	2	4	−0.11
13074.14	0	1	0.01
13060.64	6	8	0.65
13053.73			
13051.79	7	9	−0.18
13050.76	3	4	0.21
13048.30			
13039.99	0	0	−0.02
13024.66	2	2	0.06
13014.88			
12998.29	1	0	0.11
12993.74	6	6	−0.09
12975.62	4	3	0.06
12956.52	2	0	0.01
12949.07	3	1	−0.05
12920.12			
12915.11	3	0	0.11
12907.81	4	1	0.03
12866.57	5	1	−0.03
12864.76	10	7	0.15
12863.08			
12861.46			
12859.77	6	2	0.21
12857.39	11	8	−0.05
12852.45	7	3	−0.07
12850.38	12	9	0.11
12836.36	14	11	0.41
12825.67	6	1	0.08
12818.83	7	2	0.12
12811.84	8	3	0.00
12805.08	9	4	0.10
12798.18	10	5	0.05
12777.99	8	2	−0.04
12771.23	9	3	−0.10
12764.72	10	4	0.08
12757.97	11	5	0.01
12751.34	12	6	0.06
12744.65	13	7	0.04
12738.11	14	8	0.15
12731.25	15	9	−0.06
12724.40	11	4	−0.07
12724.40	16	10	−0.27
12717.89	12	5	−0.07
12711.54	13	6	0.07
12705.18	14	7	0.22
12698.17	15	8	−0.31
12691.88	16	9	−0.13
12685.54	17	10	0.00
12677.96	13	5	−0.17
12671.80	14	6	0.00
12665.60	15	7	0.12
12659.14	16	8	−0.04
12652.95	17	9	0.07
12646.68	18	10	0.09
12640.00	19	11	−0.32
12634.03	20	12	−0.03
12627.78	21	13	−0.05
12621.56	22	14	−0.03
12614.91	23	15	−0.44
12608.83	24	16	−0.31
12595.65	21	12	0.00
12589.66	22	13	0.06
12583.41	23	14	−0.14
12577.38	24	15	−0.12
12571.28	25	16	−0.18
12565.31	26	17	−0.12
12559.51	27	18	0.10
12553.20	28	19	−0.20
12545.62	24	14	−0.07
12539.80	25	15	−0.02
12533.84	26	16	−0.12
12528.08	27	17	−0.04
12522.17	28	18	−0.12
12516.19	29	19	−0.28
12510.33	30	20	−0.34
12504.68	31	21	−0.20
12498.70	32	22	−0.40
12492.89	33	23	−0.44
12490.90	28	17	−0.10
12487.18	34	24	−0.38
12485.17	29	18	−0.19
12481.36	35	25	−0.46
12479.57	30	19	−0.16
12473.83	31	20	−0.29
12468.14	32	21	−0.38
12462.51	33	22	−0.42
12456.95	34	23	−0.40
12451.42	35	24	−0.36
12445.69	36	25	−0.54
12440.29	37	26	−0.39
12435.74			
12435.01	38	27	−0.13
12432.20	33	21	−0.15
12429.17	39	28	−0.44
12423.65	40	29	−0.44
12415.86	36	24	−0.32
12414.32			
12412.50	42	31	−0.58
12410.40	37	25	−0.44
12405.12	38	26	−0.36
12399.62	39	27	−0.52
12396.09	34	21	−0.28
12394.32	40	28	−0.49
12390.53	46	35	−0.68
12388.72	41	29	−0.77
12383.52	42	30	−0.66
12378.34	43	31	−0.54
12373.08	44	32	−0.52
12367.63	45	33	−0.70
12364.89	40	27	−0.39
12362.37	46	34	−0.71
12359.76	41	28	−0.45
12357.29	47	35	−0.54
12354.57	42	29	−0.52
12351.87	48	36	−0.72
12349.42	43	30	−0.56
12346.65	49	37	−0.72
12344.21	44	31	−0.68
12341.45	50	38	−0.71
12339.13	45	32	−0.68
12336.38	51	39	−0.58
12334.07	46	33	−0.68
12331.23	52	40	−0.54
12328.97	47	34	−0.73
12325.99	53	41	−0.60
12323.94	48	35	−0.72
12318.95	49	36	−0.68
12314.12	50	37	−0.50
12308.99	51	38	−0.63
12304.08	52	39	−0.55
12300.70	47	33	−0.67
12299.00	53	40	−0.65
12295.70	48	34	−0.83
12294.05	54	41	−0.63
12290.95	49	35	−0.75
12289.21	55	42	−0.51
12286.14	50	36	−0.74
12284.29	56	43	−0.48
12281.44	51	37	−0.64
12279.56	57	44	−0.28
12276.59	52	38	−0.70
12274.80	58	45	−0.11
12271.92	53	39	−0.59
12270.02	59	46	0.03
12267.17	54	40	−0.57
12265.24	60	47	0.16
12262.51	55	41	−0.48
12260.55	61	48	0.37
12257.93	56	42	−0.31
12255.80	62	49	0.51
12253.28	57	43	−0.23
12251.30	63	50	0.89
12248.64	58	44	−0.15
12246.48	64	51	0.94
12244.13	59	45	0.05
12239.54	60	46	0.16
12235.12	61	47	0.43
12230.65	62	48	0.64
12229.71	I	1	
12226.21	63	49	0.87
12225.16	I	2	
12221.92	64	50	1.24
12220.79	I	3	
12216.48	I	4	
12213.85	60	45	0.38
12213.15	II	1	
12211.96	I	5	
12209.54	61	46	0.55
12209.00	II	2	
12207.61	I	6	
12205.38	62	47	0.86
12204.69	II	3	
12204.10	III	1	
12203.31	I	7	
12201.15	63	48	1.09
12200.51	II	4	
12199.01	I	8	
12197.02	64	49	1.41
12196.26	II	5	
12195.48	III	3	
12194.71	I	9	
12192.91	65	50	1.73
12192.11	II	6	
12191.37	III	4	
12190.53	I	10	
12188.87	IV	1	
12188.02	II	7	
12187.12	III	5	
12186.36	I	11	
12184.85	IV	2	
12183.86	II	8	
12183.14	III	6	
12182.22	I	12	
12180.89	IV	3	
12179.87	II	9	
12179.04	III	7	
12178.11	I	13	
12176.88	IV	4	
12175.83	II	10	
12175.00	III	8	
12174.12	I	14	
12173.10	IV	5	
12170.99	III	9	
12169.98	I	15	
12169.24	IV	6	
12167.13	III	10	
12163.20	III	11	
12159.32	III	12	
12157.86	V	1	
12157.19	VI	1	
12155.46	III	13	
12154.79	V	2	
12154.04	VI	2	
12151.71	III	14	
12151.71	V	3	
12150.98	VI	3	
12148.87	V	4	
12147.93	III	15	
12147.93	VI	4	
12146.40	VII	1	
12144.20	III	16	
12142.74	VII	2	
12140.41	III	17	
12139.18	VII	3	
12136.69	III	18	
12133.04	III	19	
12129.48	III	20	
12126.00	III	21	
12124.21	VIII	1	
12122.57	III	22	
12122.03	IX	1	
12120.60	VIII	2	
12119.12	III	23	
12118.42	IX	2	
12117.02	VIII	3	
12115.77	III	24	
12114.83	IX	3	
12113.81	VIII	4	
12112.34	III	25	
12109.00	III	26	
12107.55	X	1	
12105.63	III	27	
12102.23	III	28	
12101.30	X	3	
12100.23	XI	1	
12098.87	III	29	
12098.04	X	4	
12096.73	XI	2	
12095.46	III	30	
12092.06	III	31	
12088.86	III	32	
12085.92	III	33	
12082.80	III	34	
12079.56	III	35	
12078.67	XII	1	
12077.29	XIII	1	
12075.32	XII	2	
12073.97	XIII	2	
12071.95	XII	3	
12070.39	XIII	3	
12068.54	XII	4	
12065.18	XII	5	
12062.29			
12061.78	XII	6	
12061.07			
12054.98	XIV	1	
12051.57	XIV	2	
12049.59	XV	1	
12048.30	XIV	3	
12046.61	XV	2	
12043.73	XV	3	
12042.27	XIV	5	
12040.88	XV	4	

sponds to transitions to comparatively steep parts of the upper potential energy curve. Because of the limited extent of the left arm, reliable combination differences for checking the assignments to the right arm are lacking, and it is for this reason that the assignment of sequences near the red end of the system becomes ambiguous.

In Figs. 3 and 4 the vibrational intervals, ΔT, are plotted against the vibrational terms, for the lower and upper states of this system, respectively. The circles represent the experimental values; the full curves correspond to the intervals and terms calculated from Eq. (3). It will be noted that, as is usual in such cases, the last observed points begin to drop below the curves, so that the values of T' and T'' at which these curves strike the axes can be taken as maximum values for the energies of the respective products of dissociation. That is, $T_a' < 15{,}800$ cm^{-1} and $T_a'' < 4020$ cm^{-1}. On the other hand T' and T'' have already been followed as far as 14,570 cm^{-1} and 2330 cm^{-1} and are still far from convergence. It seems fairly safe to conclude that minimum values of the energies of the respective atomic products of dissociation are given by the extrapolations along the dashed curves in Figs. 3 and 4, which yield $T_a' > 15{,}050$ cm^{-1}, $T_a'' > 3300$ cm^{-1}. Now the convergences have been followed far enough to leave no doubt that, as with the other alkalis, the products of dissociation of the ground state of the molecule are two normal (6^2S) Cs atoms and that those of the upper state are a normal atom and one in the 6^2P state; but they are not sufficient to allow one to distinguish whether the excited atomic state is $6^2P_{1/2}$ or $6^2P_{3/2}$. Hence in deducing maximum and minimum values for $T_a'' = D_e''$ from the above maximum and minimum values of T_a' one must in the first case use the high frequency component, 11,732 cm^{-1}, and in the second case the low frequency component, 11,178 cm^{-1}, of the resonance doublet of caesium. These yield

$$D_e'' < 15{,}800 - 11{,}178 = 4622 \text{ cm}^{-1},$$
$$D_e'' > 15{,}050 - 11{,}732 = 3318 \text{ cm}^{-1}.$$

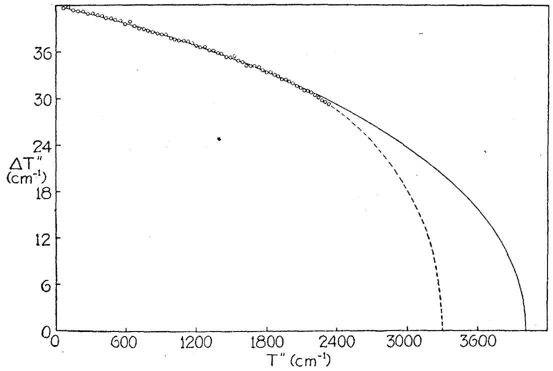

FIG. 3. $\Delta T''$ *vs.* T'' for 7667A system.

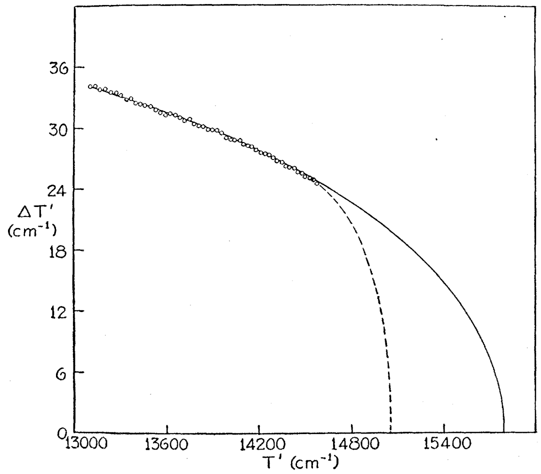

FIG. 4. $\Delta T'$ *vs.* T' for 7667A system.

Since the direct extrapolation of the ground state of the molecule yields 4020 cm$^{-1} > D_e'' > 2900$ cm^{-1} one may conclude that

$$4020 \text{ cm}^{-1} > D_e'' > 3318 \text{ cm}^{-1}$$

or

$$0.496 \text{ volt} > D_e'' > 0.410 \text{ volt},$$

and one may well take $D_e'' = 0.45$ volt as the best value and feel confident that it is not in error by more than 0.04 volt.

This value is a not unreasonable extrapolation of the heats of dissociation of the other alkalis, as can be seen from Fig. 5 in which the values of D_e'' are plotted for H_2, Li_2, Na_2, K_2 and Cs_2. The smooth curve fits all points within their limits of error. Interpolation according to the curve gives 0.47 volt as a fairly reliable value for the energy of dissociation, D_e'', of Rb_2.

Several values of D_e'' have been published, all of which are smaller than the minimum value

0.41 volt, compatible with our measurements. However, the only reliable one, by Freudenberg,[9] agrees with ours within his limits of error. Our minimum value depends on the dotted extrapolation in Fig. 4 and an inspection of this curve will show that it can hardly be subject to the general suspicion that all band spectrum extrapolations are too high. It seems worth while, however, to discuss the accuracy and validity of the results of previous observers.

Minkowski and Mühlenbruch,[10] on the basis of measurements of the variation of pressure needed to annul the effect of variation of temperature on the overall intensity of the 6250A bands, concluded that $0.24 \text{ volt} > D_e'' > 0.04$ volt. This is in conflict with our result and cannot be correct since we have already followed the vibrational levels of the ground state as far as $2330 \text{ cm}^{-1} = 0.29$ volt and are still far from convergence. Their conclusions are, however, subject to the serious error that they are based on measurements of total absorption, instead of the integral of absorption coefficients, and that the effect of increase of temperature, even when compensated by pressure variation, will be, in part, to shift the absorption from lines where it is nearly total, to higher lines where it is smaller and more nearly proportional to the absorption coefficient.

Boeckner and Mohler[11] measured the variation with temperature of the ratio between the ionization produced by atomic absorption of light of shorter wave-length than the series limit, and that produced by the assumed molecular absorption between the series lines, and concluded that $D_e'' = 0.26$ volt. Their deductions are however subject to the same source of error as Minkowski and Mühlenbruch's.

Rompe publishes values of the energy of dissociation of the ground state; but these are based on unsupported and unjustifiable interpretations as to the nature of certain bands and band systems, and need not be further considered.

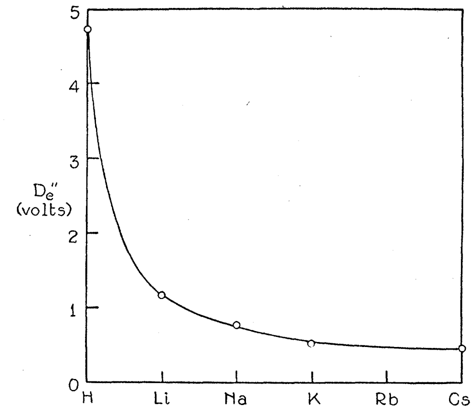

FIG. 5. Curve showing the energies of dissociation of the, elements in the alkali metal group.

Freudenberg[9] concludes, on indirect evidence, that $0.55 \text{ volt} > D_e'' > 0.15$ volt, and our value also lies between these limits but is considerably more precise. Freudenberg's value depends on his determination of the energy of activation, E, of the reaction

$$\text{Cs}'(7^2P_{3/2}) + \text{Cs}(6^2S) + E = \text{Cs}_2^+ + \text{electron}$$

as $E = 0.125 \mp 0.025$ volt, resulting from a study of the temperature dependence of photo-ionization by the 4555A, $7^2P_{3/2} \leftarrow 6^2S$ line of Cs. It also depends on his interpretation of the phenomenon observed by Boeckner and Mohler[11] that photo-ionization of caesium vapor can be caused by light not coinciding with atomic lines if its wave-length does not exceed 3800A. This effect is interpreted, both by Boeckner and Mohler and by Freudenberg, as being due to absorption of light by the neutral molecule, which is thus brought into an excited state with enough energy to auto-ionize immediately. Freudenberg concludes that J_m, the ionization potential of the caesium molecule is 3.17 ∓ 0.20 volts, corresponding to 3880A. The evidence for this interpretation, while plausible, is somewhat indirect and not absolutely conclusive. If accepted, it follows that

$$J_m = D_e'' + h\nu(4555\text{A}) + 0.125 \text{ volt} \qquad (4)$$

or $D_e'' = 3.17 - 2.71 - 0.125 = 0.33 \mp 0.2$ volt, as stated by Freudenberg. This agreement with our directly determined value of D_e'' may serve as confirmatory evidence for the above inter-

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[9] Freudenberg, Zeits. f. Physik **67**, 417 (1931).

[10] Minkowski and Mühlenbruch, Zeits. f. Physik **63**, 198 (1930).

[11] Boeckner and Mohler, Bur. Standards J. Research **5**, 831 (1930).

pretation, but a more reliable and accurate value for J_m, the ionization potential of the molecule may be deduced by reversing the argument and putting our value of D_e'' into Eq. (4), retaining Freudenberg's 0.125 ∓ 0.025 volt as the heat of activation. This yields

$$J_m=(0.45\mp 0.04)+2.71+(0.125\mp 0.025)$$
$$=3.28\mp 0.07 \text{ volts.}$$

Since this system lies on the high frequency side of the resonance lines, and since the difference of energy of the products of dissociation of the two states concerned is approximately equal to the energy of the resonance level of the atom, it is very likely that it is a $^1\Pi\leftarrow {}^1\Sigma$ transition as the corresponding systems in Li_2, Na_2 and K_2 are known to be.

XI. At 8170, 8262, 8346 and 8733A, appear four diffuse bands, degraded to the red, the last lying between the members of the resonance doublet. These may be similar to the structure around the second and third doublets of the principal series which has been reported by Kuhn.[7] On plates of higher dispersion a finer structure can be seen, closer to the resonance lines.

XII. From between the resonance lines to at least 10,500A, the limit of effective sensitivity of Eastman Q type plates, lies a strong system of numerous bands with sharp heads, degraded to the red. It seems very probable that this corresponds to the $^1\Sigma\leftarrow {}^1\Sigma$ systems which have been found on the long wave-length side of the resonance doublets in the molecules Li_2, Na_2 and K_2. The origin of this system appears to lie beyond the region we were able to photograph, so that a complete analysis was not possible. However 44 bands have been measured and 38 have been assigned to three v' progressions. Their frequencies can be represented by the equation

$$\nu=9596.5+41.66n'-0.04642n'^2-34.7n'', \quad (5)$$

in which n' and n'' presumably differ by constants from the true v' and v''. The observed frequencies, the assigned n' and n'' and the differences between the measured frequencies and those calculated from Eq. (4) are given in Table VI.

TABLE VI. *Band heads in the system to the long wave-length side of the resonance doublet.*

ν observed	n''	n'	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
10843.1			
10838.7			
10834.8			
10765.6	2	29	0.1
10731.9	1	29	1.1
10688.4	1	28	−2.9
10652.3	1	27	−0.4
10612.2	1	26	−1.3
10574.9	1	25	0.7
10535.6	1	24	0.8
10498.0	1	23	2.6
10456.3	1	22	0.5
10417.3	1	21	1.2
10378.1	1	20	1.7
10338.1	1	19	1.6
10297.0	1	18	0.4
10257.2	1	17	0.6
10216.6	1	16	0.2
10176.3	1	15	0.1
10134.8	1	14	−1.1
10127.2	0	13	−3.0
10094.5	1	13	−1.0
10086.8	0	12	−2.9
10053.7	1	12	−1.3
10047.9	0	11	−1.2
10013.7	1	11	−0.7
10012.5			
9973.2	1	10	−0.5
9971.8			
9967.3	0	9	−0.4
9931.3	1	9	−1.7
9926.7	0	8	−0.1
9891.3	1	8	−0.8
9886.3	0	7	0.5
9851.0	1	7	−0.1
9845.3	0	6	0.5
9809.7	1	6	−0.4
9768.0	1	5	−0.9
9728.2	1	4	0.5
9689.0	1	3	2.6
9644.8	1	2	−0.1
9603.5	1	1	0.1
9567.5	2	1	−1.3
9562.4	1	0	0.6

The v' levels of this system converge very slowly, so that their extrapolation to convergence, which according to Eq. (5) occurs at 19,000 cm^{-1}, is extremely unsafe, but since such long extrapolations almost always give values which are too high, it is entirely reasonable to assume that the products of dissociation of the upper state of this system are, by analogy with similarly located bands of Li_2, Na_2 and K_2, a normal Cs atom and one in the resonance state, in which case the true convergence point would be 15,500 cm^{-1} or less.

A letter in *Nature* by Matuyama[12] has just appeared in which measurements on caesium bands are also reported. In general his measurements are less accurate and his analysis less complete than ours, and he does not get a value for the energy of dissociation. The points of agreement and disagreement are as follows: (1) His equation for the 7667A system is, as far as it goes, roughly equivalent to ours, but he assigns only 38 bands to it, while we have assigned 211 bands, which has enabled us to extrapolate to dissociation. (2) His equation for the 6250A system is somewhat like ours, but his value for ω'' of the lower state of this system differs from that of the 7667A system, while our analysis makes it accurately the same and, since it agrees also with the fluorescence interval, justifies its interpretation as the ground level. (3) He reports the lower and upper vibrational

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[12] Matuyama, Nature **133**, 568 (1934).

intervals of the 7200A system as 39 and 29 cm^{-1}, based on measurements of 16 heads. We have taken them as 49.5 and 38.5 cm^{-1}, based on measurements of 10 heads, but convergence is not appreciable and it would also have been possible to assign them as Matuyama has done. This would have given equally good combination differences but the arrangement into a square array would have been abnormal. (4) We believe that the band system which he reports at 8200A is merely the red end of the 7667A system, after it has been interrupted by the diffuse bands at 8170, 8262 and 8346A. We have measured the bands in this region and reported them as unassigned sequences in Table V. (5) Matuyama also notes the existence of the new system XII.

Band Systems of BaCl

Allan E. Parker, *Columbia University and Yale University*

(Received May 21, 1934)

Three band systems of BaCl have been analyzed by means of spectrograms taken in the second order of two 21 foot gratings. The green system (λ5047 to λ5322) is a $^2\Pi-{}^2\Sigma$ transition and due to the nearly equal values of ω for the two electronic states is composed of only the $\Delta v=0, \pm 1$ sequences. There are two ultraviolet systems with (0,0) bands at λ3922 and λ3692, respectively. Both are presumably $^2\Sigma-{}^2\Sigma$ transitions and have broader Franck-Condon parabolas than the green system. The isotope effect of Cl^{35} and Cl^{37} is observed but in none of the systems could any bands be definitely attributed to barium isotopes other than Ba^{138}. The dissociation products are discussed.

Introduction

The existence of bands due to BaCl has been known for some time.[1, 2] Two groups of bands were observed by King and Harnack. There is an extremely intense system in the green extending from λ5047 to λ5322. The other group is in the ultraviolet and extends from λ4005 to λ3555. This group is composed of two systems which are much weaker than the green system. Hedfeld[3] photographed the green system with a 12 foot grating, burning BaCl$_2$ in an oxy-acetylene flame, and made an assignment of certain of the bands. Schaafsma[4] also photographed these bands using an arc in a hydrogen atmosphere. He attempted unsuccessfully to assign them to a $^2\Sigma-{}^2\Sigma$ transition of BaH. The present work shows quite conclusively that this is not correct, since it is quite evident upon spectrograms taken with sufficient dispersion and intensity that what Schaafsma refers to as lines are really band heads. Furthermore the isotope effect of Cl^{35} and Cl^{37} is observed. This will be discussed in more detail later in the paper. The present analysis confirms that of Hedfeld in the main, though differing in several essentials, and it extends his analysis considerably, assigning several hundred bands instead of some thirty to forty. The analysis of the ultraviolet bands had not been previously attempted.

Experimental Details

To excite the bands a method quite similar to that of Schaafsma was used. An arc was formed in a bulb between a water-cooled nickel anode and a copper cathode in the form of a cup, the cup containing BaCl$_2$. The bulb was filled with hydrogen to a pressure of 5–10 cm of mercury. The bands were obtained with approximately the same intensity if nitrogen was used instead of hydrogen, showing that the bands were undoubtedly not BaH. Also these bands were not obtained from an arc between barium electrodes in a hydrogen atmosphere. All spectrograms measured were taken with hydrogen in the bulb as they were much "cleaner."

Spectrograms of the various BaCl bands were obtained in the second order of the 21 foot

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[1] A. S. King, Astrophys. J. **21**, 236 (1905).

[2] A. Harnack, Dissertation, Leipzig (1911).

[3] K. Hedfeld, Zeits. f. Physik **68**, 610 (1931).

[4] A. Schaafsma, Dissertation, Groningen (1932).

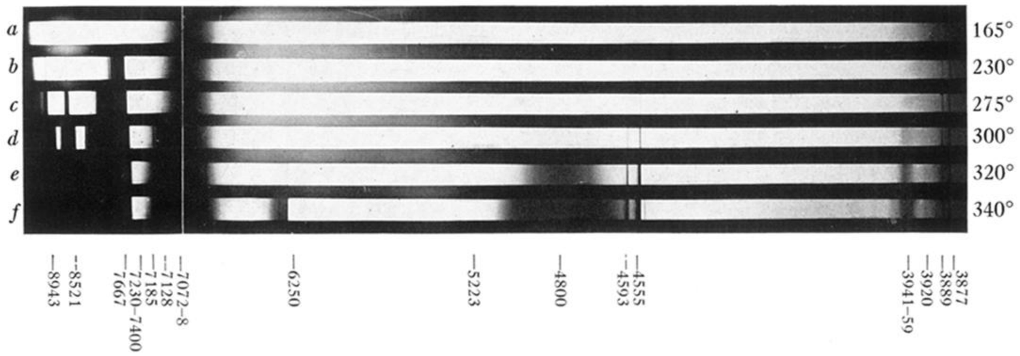

FIG. 1A.

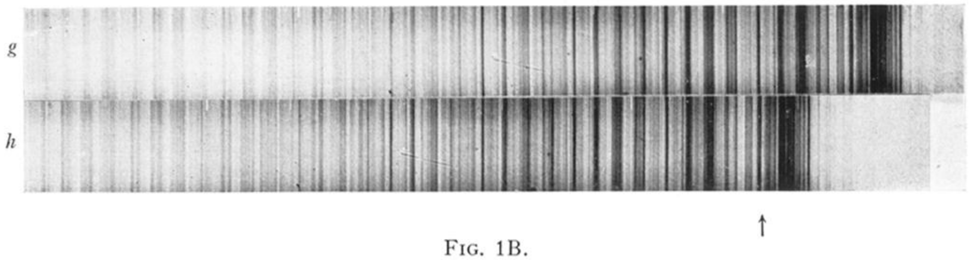

FIG. 1B.

FIG. 1. The band spectra of Cs_2. The spectrograms on the left, *a–f*, were taken on an Eastman 3P plate; those to the right on an Eastman hypersensitive panchromatic plate.