THE MOLECULAR SPECTRA OF CAESIUM AND RUBIDIUM

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY POLYKARP KUSCH

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THE MOLECULAR SPECTRA OF CAESIUM AND RUBIDIUM.

I. INTRODUCTION.

The molecular spectra of the alkali metals have been known for a long time. Rather complete information is already available with regard to the vibrational structure of the electronic bands of Li_2, Na_2 and K_2. The best vibrational analyses have been made by Loomis and Nusbaum,[1,2,3] who used the method of magnetic rotation. From these data they have obtained accurate values for the heats of dissociation of Li_2, Na_2 and K_2. Further information about these three molecules has been obtained from observations of their absorption spectra.

The data available on the molecular spectra of Rb_2 and Cs_2 are much more limited. Walter and Barratt[4] have reported the wave lengths of some bands in the spectra of both of these molecules but no attempt at analysis has been made. Rompe[5] has extended the data on Cs_2, but his data are incomplete and the analysis is inadequate. Matuyama[6] has observed the molecular spectrum of Cs_2 in some detail, but the data are insufficient for the determination of the energy of dissociation. Matuyama[7] has further observed the molecular spectrum of Rb_2, but here again the work is incomplete.

II. THE PURPOSE OF THIS INVESTIGATION.

This investigation was undertaken to extend our knowledge of the spectra and heats of dissociation of the alkali metal molecules to those members of the series for which complete data are not already 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. This transition may be expected to occur for the last two members of the alkali metal series, and it is

one purpose of this investigation to see if such a transition may be detected.

III. EXPERIMENTAL METHOD.

The molecular spectra of caesium and of rubidium were observed in absorption, in magnetic rotation and in fluorescence. Because of the fact that both caesium and rubidium are expensive, and because they are very difficult to prepare, it was not feasible to use a metal tube with waxed on windows as an absorption tube as Loomis and Nusbaum[1] did in their work on lithium, sodium and potassium. Such a tube has the advantage of enabling one to work at much higher temperatures than are available with glass tubes, but they require a large amount of the substance to be investigated, and involve a considerable wastage of the substance. All of the present work was therefore done in glass absorption tubes.

The caesium and rubidium were prepared in an identical manner from the corresponding chloride. A few grams of the chloride were dried by heating in a stream of HCl. The dry chloride was then intimately mixed with an excess of finely powdered calcium. The calcium was freshly ground from a lump of metallic calcium by means of a file, just before it was to be used. The mixture was placed in a heavy pyrex combustion tube which had been sealed off at one end. A plug of calcium shavings was then placed in the combustion tube to prevent dust from the chloride mixture from blowing into the absorption tube. The combustion tube was placed in a horizontal position in a gas furnace and sealed to a pumping system and to the absorption tube. No rubber or wax joints were used in any part of the system.

The absorption tube was heated to a temperature of about 250°C. while it was being pumped to a high vacuum. This removed any traces of water as well as occluded gases from the inside of the tube. At the same time the combustion tube was gently heated to drive the gases from the mixture.

When a very high vacuum had been obtained the temperature of the combustion tube was raised till the caesium or rubidium began to distill off very slowly. The metal condensed in the relatively cool region of the combustion tube just out-

side the furnace. From time to time this metal was driven into the absorption tube, which had been allowed to cool, by heating with a torch. This constituted, essentially, a series of distillations, so that the metal in the tube was quite free of impurities whose vapour pressures differed greatly from those of the metal.

The glass absorption tubes thus prepared could be kept at 300°C. for long periods of time, without appreciable blackening. At temperatures above 325°C, the inner surface of the tube blackened very quickly.

For the absorption measurements the absorption tubes were about 30 inches long and an inch and a half in diameter.

For the work in magnetic rotation, special absorption tubes were required, since it was necessary that extinction of a beam of light be obtained when it was passed through the tube, placed between crossed nicol prisms. The windows were sealed to short sections of glass tubing of the same diameter as the absorption tube. These sections were then carefully annealed to relieve the strains introduced in the windows by the process of fusing the windows to the tubes. The success of the method seems to depend on a careful annealing, for the presence of strains in the windows makes it impossible to obtain extinction when the tube is placed between crossed nicols. The small sections of the tube thus annealed were finally sealed to the central portion of the absorption tube.

The tube used in the fluorescence work consisted of a glass tube, about 30 inches long, one end of which was drawn into a horn shaped figure, and to the other end of which a plane glass window was sealed.

For the work in absorption the tube was placed in a long brass tube about which a solenoid of German silver wire had been wound. Some extra wire was wound near the end of the furnace to keep the windows of the absorption tube slightly hotter than the rest of the tube and thus prevent condensation of the metal on the windows. The ends of the brass tube were closed with asbestos boards on which windows had been mounted. These served to keep convection currents out of the furnace. Temperatures were measured by means of a Chromel-Alumel thermocouple.

The same apparatus was used for the observation of the magnetic rotation

spectrum that Loomis and Nusbaum[1] used for their investigations of the other alkali metals. The nickel tube which they used was replaced by the special glass tube. Heating was accomplished by a heating coil wound directly on the glass tube, and, as before provision was made to keep the metal from condensing on the windows of the tube.

Attempts were also made to find fluorescence spectra of caesium. Unfortunately there is a dearth of strong lines, suitable for excitation, in the regions 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[8] technique, yielded a series of fluorescence lines excited by Ne 6402 A.

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 1.3 A/mm. in the first order. This proved necessary to effect satisfactory resolution of the vibrational structure in many regions; in no region was it adequate to resolve the rotational structure.

The magnetic rotation spectra were observed on a Hilger E 1 spectrograph with glass parts.

The fluorescence spectra were observed on a Hilger E 63 spectrograph.

IV. RESULTS AND ANALYSES.

1. Caesium.

All the features observed in the absorption spectrum of caesium in the range 3880 - 10,500 A are discussed below.

I. At the short wave length end of this region is the 3877, 3889 A, $8^2P \leftarrow 6^2S$ doublet of the principal series, in which, at high temperatures, the structure reported by Kuhn[9] and explained by him in terms of polarization molecules, becomes apparent.

II. At 3920 A 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 3961 A appears at 270°C. and at higher temperatures can be clearly seen on my original plates to contain four heads, degraded to short wave-lengths, at 3941, 3947, 3953 and 3959 A and to be accompanied, on the long wave-length side by faint diffuse maxima at approximately 3983, 4006, 4035 and 4065 A. 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 4315 A, and which faintly appears on my plates.

IV. In the neighborhood of the 4555, 4593 A, $7^2P \leftarrow 6^2S$ 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 4800 A. With increasing temperature this system spreads out in both directions. On the short wave-length side, it approaches, and perhaps finally crosses, the 4555, 4593 A doublet. On the long wave-length side it terminates rather abruptly at high temperatures in an edge at 5223 A which appears very similar to the infrared edge reported and explained by Loomis and Nile[10] 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 I have found is by Walter and Barratt[4] who call it a diffuse band with an edge, on the red end, at 5224 A. 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 it has not been possible to make 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 I 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 I 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 7667 A system.

Table I.

Band heads in the system of caesium at 4800 A.

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		

VI. At about 360° a very faint system, not previously reported, begins to appear near 5600 A. It 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 6250 A. 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.

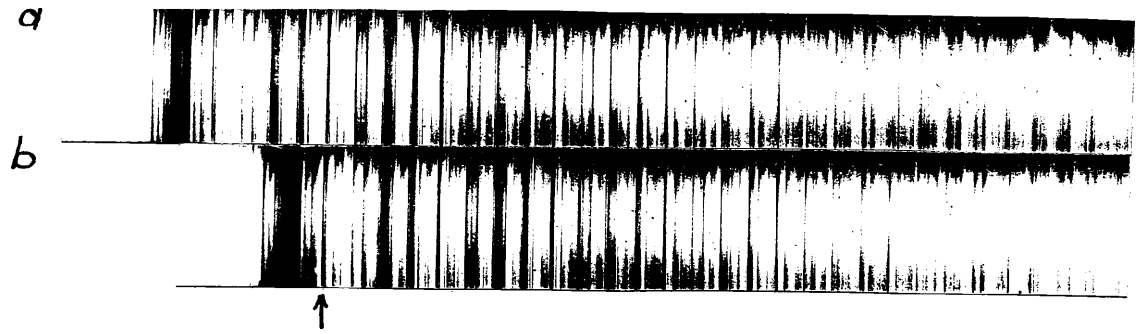

Fig. 1. The 6250 A band system of caesium.

VII. At about 230°C. a prominent, but very complex, band system appears near 6250 A. 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 6550 A. This system has been reported by Rompe[5] and by Matuyama[6], who has given an analysis for the system. It appears in Fig. 1, a and b, 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. A complete analysis or understanding of this system, or systems, has not been attained but some regularities have been uncovered.

The 6402 A 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 7667 A. With this as a basis, the heads of 31 bands, all degraded to the blue, have been assigned to a square

Table II.

Fluorescence series in the 6250 A system of caesium excited by the 6402 A 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	

array. Their frequencies can be expressed by the formula

$$\nu = 16066.03 + 29.38(n' + \tfrac{1}{2}) - 0.0796(n' + \tfrac{1}{2})^2 - \left[41.990\ (v'' + \tfrac{1}{2}) - 0.080051(v'' + \tfrac{1}{2})^2 - 0.000164266(v'' + \tfrac{1}{2})^3\right], \qquad (1)$$

in which the lower vibration interval agrees with that of the 7667 A 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.

It has been possible to find several progressions among the bands degraded to the red and to assign the quantum numbers of the lower state to the bands in these progressions by reference to the accurately known ground of caesium. These progressions have been fitted into a square array. As was the case with the

Table III.

Blue degraded band heads in the system of caesium at 6250 A.

ν observed	I	v"	n'	$\nu_{obs.} - \nu_{calc.}$	ν observed	I	v"	n'	$\nu_{obs.} - \nu_{calc.}$
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					

bands in this system, degraded to the blue, it has been impossible to follow the system to its origin and therefore to assign quantum numbers to the upper state. Matuyama[6] reports an origin of the system at 15,901 cm^{-1} but this assignment is believed to be incorrect. For, certain of Matuyama's progressions may be identified with mine, but the quantum numbers of the ground state which he assigns to the bands in the progressions differ from the true quantum numbers as determined from the known ground state. Furthermore, a large number of the bands assigned by Matuyama cannot be assigned into such an array, while keeping the combination differences constant within experimental error.

The bands, degraded to the red, which have been assigned into a square

array are accurately represented by the formula

$$\nu = 16{,}175.80 + 27.34(n' + \tfrac{1}{2}) - 0.0733(n' + \tfrac{1}{2})^2 - \left[41.990(v'' + \tfrac{1}{2}) - 0.080051(v'' + \tfrac{1}{2})^2 - 0.000164266(v'' + \tfrac{1}{2})^3\right], \quad (2)$$

v" is the true quantum number, and n' differs from the true v' by some unknown constant. The ground state is identical to that of the 7667 A system. The observed band heads, their intensities, assignments and the differences between the observed values and those given by Eq. (2) are given in Table IV.

Table IV.

Red degraded band heads in the system of caesium at 6250 A.

i	ν observed	n'	v"	$\nu_{obs} - \nu_{calc.}$	i	ν observed	n'	v"	$\nu_{obs} - \nu_{calc.}$
2	16054.05	5	6	-0.39	8	15971.19	8	10	+0.18
2	16029.17	1	4	-0.16	5	15960.55	0	5	-0.40
1	16027.87	4	6	+0.03			3	7	+0.31
3	16025.26	7	8	-0.44	6	15946.98	1	6	-0.16
2	16015.43	2	5	+0.24	7	15946.33	4	8	+0.01
4	16013.27	5	7	-0.33	4	15945.01	7	10	+0.16
4	16011.81	8	9	-0.46	9	15932.13	5	9	-0.28
4	16001.78	0	4	-0.35	4	15930.82	8	11	-0.02
2	16000.47	3	6	-0.61	1	15919.24	3	8	-0.32
4	15999.03	6	8	-0.35	5	15918.18	6	10	-0.35
5	15988.30	1	5	+0.15	0	15905.99	4	9	+0.19
4	15986.82	4	7	-0.18	4	15904.46	7	11	-0.22
3	15985.01	7	9	-0.18	4	15892.00	5	10	-0.07
1	15974.73	2	6	+0.55	5	15890.70	8	12	-0.14
4	15972.56	5	8	-0.36	7	15878.15	6	11	-0.23

(Table IV. continued on page 11)

Table IV. (continued)

i	ν observed	n'	v"	$\nu_{obs} - \nu_{calc.}$	i	ν observed	n'	v"	$\nu_{obs} - \nu_{calc.}$
3	15877.33	9	13	+0.29			8	15	-0.06
9	15864.49	7	12	-0.19	6	15758.96	6	14	+0.08
5	15861.60	5	11	-0.30	7	15758.54	9	16	-0.04
7	15860.82	8	13	-0.20	6	15745.44	7	15	-0.29
8	15837.47	9	12	+0.09			10	17	+0.08
10	15824.70	7	13	-0.15	8	15732.42	8	16	-0.15
3	15824.05	10	15	+0.26	7	15719.45	9	17	-0.03
4	15811.85	5	12	-0.05	6	15706.45	10	18	+0.04
6	15811.06	8	14	-0.30	4	15693.40	8	17	-0.06
5	15797.92	9	15	+0.01	6	15680.62	9	18	-0.01
4	15785.21	7	14	+0.01	5	15667.79	10	19	+0.15
4	15784.50	10	16	+0.02	4	15654.75	11	20	-0.03
9	15771.83	5	13	-0.25	4	15641.78	9	19	+0.02
					4	15629.31	10	20	+0.26

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, a and b 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, alike, even to the finer details.

VIII. At 7072, 7075 and 7078 A there are three sharp edges, degraded to the blue, which appear as a single diffuse band under low dispersion, 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 7185 A.

IX. The strongest system of the entire spectrum, with its origin at 7667 A, 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 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. I 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 (X); 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

$$\begin{aligned}\nu = {} & 13{,}043.87 + 34.230(v' + \tfrac{1}{2}) \\ & - 0.077936(v' + \tfrac{1}{2})^2 - 0.000188149(v' + \tfrac{1}{2})^3 \\ & - \left[41.990(v'' + \tfrac{1}{2}) - 0.080051(v'' + \tfrac{1}{2})^2 \right. \\ & \qquad \left. -0.000164266(v'' + \tfrac{1}{2})^3 \right]. \end{aligned} \qquad (3)$$

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 Franck-Condon diagram for the 7667 A 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

Table V.

Band heads in the system of caesium at 7667 A.

ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$	ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$
13372.42	10	23	0.34	13292.32	15	27	-0.37
13362.56	11	24	0.44	13291.53			
13352.55	12	25	0.40	13290.81	2	10	0.29
13342.30	13	26	0.14	13290.19	9	19	0.45
13332.99	14	27	0.82	13288.40			
13328.87				13287.15			
13327.55	5	15	0.27	13286.80	6	15	0.52
13325.36				13284.45			
13323.71	2	11	0.69	13283.61			
13322.58	12	24	0.46	13282.60	13	24	0.31
13322.58	16	28	0.42	13281.98	3	11	0.47
13321.23	9	20	0.55	13277.30	7	16	0.24
13318.47	6	16	0.55	13263.61	5	13	0.13
13311.07	10	21	-0.03	13254.63	6	14	0.17
13308.33	7	17	-0.22	13249.15	3	10	0.14
13305.02	4	13	0.36	13249.15	10	19	-0.25
13302.32	14	26	-0.19	13240.45	4	11	0.28
13299.43	8	18	0.29	13236.66	8	16	0.28
13298.80				13222.84	6	15	0.37
13298.24				13221.01			
13297.70				13219.13	10	18	0.84
13297.22				13216.82	3	9	0.47
13295.86	5	14	0.39	13213.68	7	14	0.07
13294.35				13209.52	0	5	0.47
13292.32	12	23	0.41	13209.52	11	19	0.29

(continued on page 14)

Table V.

ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$	ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$
13208.11	4	10	0.44	13125.79	6	10	0.31
13205.07	8	15	0.33	13108.17	0	2	0.07
13203.89				13100.12	1	3	0.04
13200.84	1	6	0.30	13091.95	2	4	-0.11
13199.33	5	11	0.34	13074.14	0	1	0.01
13193.61				13060.64	6	8	0.65
13192.18	2	7	0.15	13053.73			
13190.51	6	12	0.20	13051.79	7	9	-0.18
13187.36	10	17	0.36	13050.76	3	4	0.21
13183.91	3	8	0.39	13048.30			
13181.75	7	13	0.13	13039.99	0	0	-0.02
13180.07				13024.66	2	2	0.06
13178.31	11	18	0.19	13014.88			
13176.97				12998.29	1	0	0.11
13175.43	0	4	-0.13	12993.74	6	6	-0.09
13175.43	4	9	0.42	12975.62	4	3	0.06
13175.03	8	14	0.10	12956.52	2	0	0.01
13167.26	1	5	0.04	12949.07	3	1	-0.05
13163.26				12920.12			
13161.11				12915.11	3	0	0.11
13159.02	2	6	0.15	12907.81	4	1	0.03
13142.66	4	8	0.48	12866.57	5	1	-0.03
13133.88	1	4	0.15	12864.76	10	7	0.15
13133.88	5	9	0.05	12863.08			
13131.70	9	14	-0.72	12861.46			
13125.79	2	5	0.24	12859.77	6	2	0.21

(continued on page 15)

Table V.

ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$	ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$
12857.39	11	8	-0.05	12671.80	14	6	0.00
12852.45	7	3	-0.07	12665.60	15	7	0.12
12850.38	12	9	0.11	12659.14	16	8	-0.04
12836 36	14	11	0.41	12652.95	17	9	0.07
12825.67	6	1	0.08	12646.68	18	10	0.09
12818.83	7	2	0.12	12640.00	19	11	-0.32
12811.84	8	3	0.00	12634.03	20	12	-0.03
12805.08	9	4	0.10	12627.78	21	13	-0.05
12798.18	10	5	0.05	12621.56	22	14	-0.03
12777.99	8	2	-0.04	12614.91	23	15	-0.44
12771.23	9	3	-0.10	12608.83	24	16	-0.31
12764.72	10	4	0.08	12595.65	21	12	0.00
12757.97	11	5	0.01	12589.66	22	13	0.06
12751.34	12	6	0.06	12583.41	23	14	-0.14
12744.65	13	7	0.04	12577.38	24	15	-0.12
12738.11	14	8	0.15	12571.28	25	16	-0.18
12731.25	15	9	-0.06	12565.31	26	17	-0.12
12724.40	11	4	-0.07	12559.51	27	18	0.10
12724.40	16	10	-0.27	12553.20	28	19	-0.20
12717.89	12	5	-0.07	12545.62	24	14	-0.07
12711.54	13	6	0.07	12539.80	25	15	-0.02
12705.18	14	7	0.22	12533.84	26	16	-0.12
12698.17	15	8	-0.31	12528.08	27	17	-0.04
12691.88	16	9	-0.13	12522.17	28	18	-0.12
12685.54	17	10	0.00	12516.19	29	19	-0.28
12677.96	13	6	-0.17	12510.33	30	20	-0.34

(continued on page 16)

Table V.

ν observed	v''	v'	$\nu_{obs.} - \nu_{calc.}$	ν observed	v''	v'	$\nu_{obs.} - \nu_{calc.}$
12504.68	31	21	-0.20	12396.09	34	21	-0.28
12498.70	32	22	-0.40	12394.32	40	28	-0.49
12492.39	33	23	-0.44	12390.53	46	35	-0.68
12490.90	28	17	-0.10	12388.72	41	29	-0.77
12487.18	34	24	-0.38	12383.52	42	30	-0.66
12485.17	29	18	-0.19	12378.34	43	31	-0.54
12481.36	35	25	-0.46	12373.08	44	32	-0.52
12479.57	30	19	-0.16	12367.63	45	33	-0.70
12475.83	31	20	-0.29	12364.89	40	27	-0.39
12468.14	32	21	-0.38	12362.37	46	34	-0.71
12462.51	33	22	-0.42	12359.76	41	28	-0.45
12456.95	34	23	-0.40	12357.29	47	35	-0.54
12451.42	35	24	-0.36	12354.57	42	29	-0.52
12445.69	36	25	-0.54	12351.87	48	36	-0.72
12440.29	37	26	-0.39	12349.42	43	30	-0.56
12435.74				12346.65	49	37	-0.72
12436.01	38	27	-0.13	12344.21	44	31	-0.68
12432.20	33	21	-0.15	12341.45	50	38	-0.71
12429.17	39	28	-0.44	12339.13	45	32	-0.68
12423.65	40	29	-0.44	12336.38	51	39	-0.58
12415.86	36	24	-0.32	12334.07	46	33	-0.68
12414.32				12331.23	52	40	-0.54
12412.50	42	31	-0.58	12328.97	47	34	-0.73
12410.40	37	25	-0.44	12325.99	53	41	-0.60
12406.12	38	26	-0.36	12323.94	48	35	-0.72
12399.62	39	27	-0.52	12318.96	49	36	-0.68

(continued on page 17)

Table V.

ν observed	v''	v'	$\nu_{obs.}-\nu_{calc.}$	ν observed	v''	v'	$\nu_{obs.}-\nu_{calc.}$
12314.12	50	37	-0.50	12246.48	64	51	0.94
12308.99	51	38	-0.63	12244.13	59	45	0.50
12304.08	52	39	-0.55	12239.54	60	46	0.16
12300.70	47	33	-0.67	12235.12	61	47	0.43
12299.00	53	40	-0.65	12230.65	62	48	0.64
12295.70	48	34	-0.83	12229.71	I	1	
12294.05	54	41	-0.63	12226.21	63	49	0.87
12290.95	49	35	-0.75	12225.16	I	2	
12289.21	55	42	-0.51	12221.92	64	50	1.24
12286.14	50	36	-0.74	12220.79	I	3	
12284.29	56	43	-0.48	12216.48	I	4	
12281.44	51	37	-0.64	12213.85	60	45	0.38
12279.56	57	44	-0.28	12213.15	II	1	
12276.59	52	38	-0.70	12211.96	I	5	
12274.80	58	45	-0.11	12209.54	61	46	0.55
12271.92	53	39	-0.59	12209.00	II	2	
12270.02	59	46	0.03	12207.61	I	6	
12267.17	54	40	-0.57	12205.38	62	47	0.86
12265.24	60	47	0.16	12204.69	II	3	
12262.61	55	41	-0.48	12204.10	III	1	
12260.55	61	48	0.37	12203.31	I	7	
12257.93	56	42	-0.31	12201.15	63	48	1.09
12255.80	62	49	0.51	12200.51	II	4	
12253.28	57	43	-0.23	12199.01	I	8	
12251.30	63	50	0.89	12197.02	64	49	1.41
12248.64	58	44	-0.15	12196.26	II	5	

(continued on page18)

Table V.

ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$	ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$
12195.48	III	3		12167.13	III	10	
12194.71	I	9		12163.20	III	11	
12192.91	65	50	1.73	12159.52	III	12	
12192.11	II	6		12157.86	V	1	
12191.37	III	4		12157.19	VI	1	
12190.53	I	10		12155.46	III	13	
12188.87	IV	1		12154.79	V	2	
12188.02	II	7		12154.04	VI	2	
12187.12	III	5		12151.71	III	14	
12186.36	I	11		12151.71	V	3	
12184.85	IV	2		12150.98	VI	3	
12183.86	II	8		12148.87	V	4	
12183.14	III	6		12147.93	III	15	
12182.22	I	12		12147.93	VI	4	
12180.89	IV	3		12146.40	VII	1	
12179.87	II	9		12144.20	III	16	
12179.04	III	7		12142.74	VII	2	
12178.11	I	13		12140.41	III	17	
12176.88	IV	4		12139.18	VII	3	
12175.83	II	10		12136.69	III	18	
12175.00	III	8		12133.04	III	19	
12174.12	I	14		12129.48	III	20	
12173.10	IV	5		12126.00	III	21	
12170.99	III	9		12124.21	VIII	1	
12169.98	I	15		12122.57	III	22	
12169.24	IV	6		12122.03	IX	1	

(continued on page 19)

Table V.

ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$	ν observed	v"	v'	$\nu_{obs.}-\nu_{calc.}$
12195.48	III	5		12167.13	III	10	
12194.71	I	9		12163.20	III	11	
12192.91	65	50	1.73	12159.32	III	12	
12192.11	II	6		12157.86	V	1	
12191.37	III	4		12157.19	VI	1	
12190.53	I	10		12155.46	III	13	
12188.87	IV	1		12154.79	V	2	
12188.02	II	7		12154.04	VI	2	
12187.12	III	5		12151.71	III	14	
12186.36	I	11		12151.71	V	3	
12184.85	IV	2		12150.98	VI	3	
12183.86	II	8		12148.87	V	4	
12183.14	III	6		12147.93	III	15	
12182.22	I	12		12147.93	VI	4	
12180.89	IV	3		12146.40	VII	1	
12179.87	II	9		12144.20	III	16	
12179.04	III	7		12142.74	VII	2	
12178.11	I	13		12140.41	III	17	
12176.88	IV	4		12139.18	VII	3	
12175.83	II	10		12136.69	III	18	
12175.00	III	8		12133.04	III	19	
12174.12	I	14		12129.48	III	20	
12173.10	IV	5		12126.00	III	21	
12170.99	III	9		12124.21	VIII	1	
12169.98	I	15		12122.57	III	22	
12169.24	IV	6		12122.03	IX	1	

(continued on page 19)

Table V.

ν observed	v''	v'	$\nu_{obs.} - \nu_{calc.}$	ν observed	v''	v'	$\nu_{obs.} - \nu_{calc.}$
12120.60	VIII	2		12082.80	III	34	
12119.12	III	23		12079.56	III	35	
12118.42	IX	2		12078.67	XII	1	
12117.02	VIII	3		12077.29	XIII	1	
12115.77	III	24		12075.32	XII	2	
12114.83	IX	3		12073.97	XIII	2	
12113.81	VIII	4		12071.95	XII	3	
12112.34	III	25		12070.39	XIII	3	
12109.00	III	26		12068.54	XII	4	
12107.55	X	1		12065.18	XII	5	
12105.63	III	27		12062.29			
12102.23	III	28		12061.78	XII	6	
12101.30	X	3		12061.07			
12100.23	XI	1		12054.98	XIV	1	
12098.87	III	29		12051.57	XIV	2	
12098.04	X	4		12049.59	XV	1	
12096.73	XI	2		12048.30	XIV	3	
12095.46	III	30		12046.61	XV	2	
12092.06	III	31		12043.73	XV	3	
12088.86	III	32		12042.27	XIV	5	
12085.92	III	33		12040.88	XV	4	

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 corresponds 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.

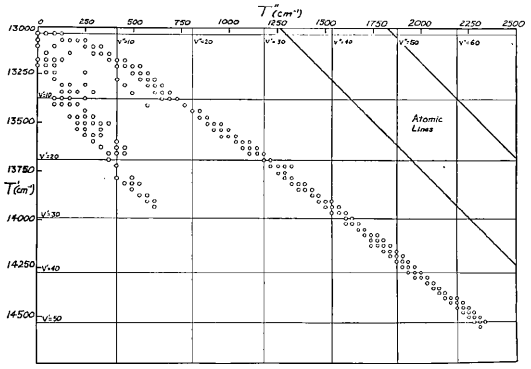

Fig. 2. Improved Franck-Condon diagram for the 7667 A system of caesium.

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 conver-

gence. 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

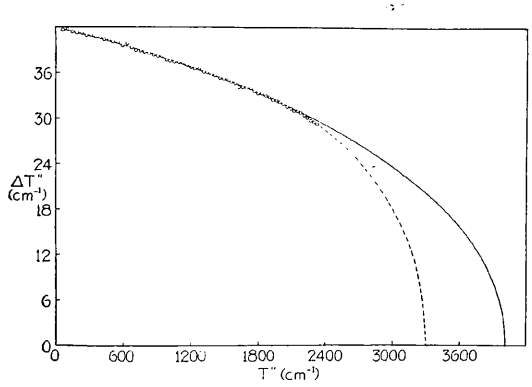

Fig. 3. $\Delta T''$ vs. T'' for 7667 A system of caesium.

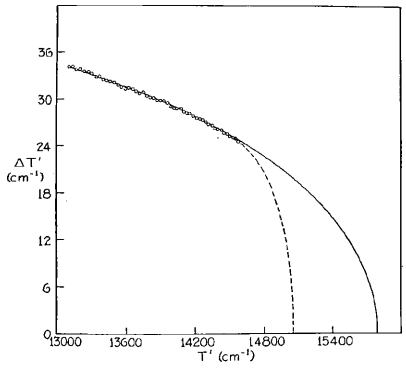

Fig. 4. $\Delta T'$ vs. T' for 7667 A system of caesium.

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 $6^2P_{\frac{1}{2}}$ 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

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

Since the direct extrapolation of the ground state of the molecule yields $4020 \text{ cm}^{-1} > D_e'' > 2900 \text{ cm}^{-1}$ 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''

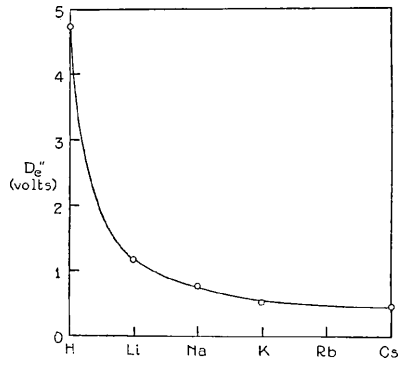

Fig. 5. Curve showing the energies of dissociation of the elements in the alkali group.

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 my measurements. However, the only reliable one, by Freudenberg,[11] agrees with mine within his limits of error. The 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,[12] 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 6250 A bands, concluded that 0.24 volt $> D_e'' >$ 0.04 volt. This is in conflict with my result and cannot be correct since the vibrational levels of the ground state have already been followed as far as 2330 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[13] 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.

Freudenberg[11] concludes, on indirect evidence, that 0.55 volt $> D_e'' >$ 0.15 volt, and my 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

$$Cs'(7^2P_{3/2}) + Cs(6^2S) + E = Cs_2^+ + \text{electron}$$

as $E = 0.125 \mp 0.025$ volt, resulting from a study of the temperature dependence of photo-ionization by the 4555 A, $7^2P_{3/2} \leftarrow 6^2S$ line of Cs. It also depends on his interpretation of the phenomenon observed by Boeckner and Mohler[13] that photo-ionization of caesium vapor can be caused by light not coinciding with atomic lines if its wave-length does not exceed 3800 A. 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 3880 A. The evidence for this interpretation, while plausible, is somewhat indirect and not absolutely conclusive. If accepted, it follows that

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

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

X. At 8170, 8262, 8346 and 8733 A, 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.[9] On plates of higher dispersion a finer structure can be seen, closer to the resonance lines.

XI. From between the resonance lines to at least 10,500 A, 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

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

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.

The v' levels of this system converge very slowly, so that their extrapolation to convergence, which according to Eq. (5) occurs at 19,000cm^{-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.

An attempt was made to find a magnetic rotation spectrum of Cs_2, to aid in the analysis. Long exposures were 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

Table VI.

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

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

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.

2. Rubidium.

The magnetic rotation spectrum and the absorption spectrum of Rb_2 in the region 6500-7100 A have been observed and measured; the two spectra have been correlated and a vibrational analysis made, in the usual way. The magnetic rotation spectrum extends further than the absorption spectrum, and is more completely developed. This is in accord with the usual experience with magnetic rotation spectra, which have, for this reason, been found to be ideal for extending a band system to the high quantum numbers necessary for the determination of an accurate energy of dissociation. The data are, however, in this case, still not extensive enough to yield a reliable value of the energy of dissociation.

Rubidium has two isotopes, Rb^{85} and Rb^{87} which occur in about the ratio 3 : 1. The three molecules $Rb^{85}Rb^{85}$, $Rb^{85}Rb^{87}$ and $Rb^{87}Rb^{87}$ should therefore have the relative concentrations 9 : 6 : 1. The bands due to $Rb^{85}Rb^{85}$ and $Rb^{85}Rb^{87}$ may be expected to be of comparable intensity. Now in these magnetic rotation spectra the most prominent features are the strong lines just to the violet of each head, the rest of the spectrum being obscured by reabsorption. Hence presumably the heads measured belong to the molecule $Rb^{85}Rb^{85}$ or $Rb^{85}Rb^{87}$ according to which has the shorter wave-length. In the case of rubidium, then, the observed lines in magnetic rotation should correspond to the band heads due to the molecule $Rb^{85}Rb^{85}$ at the short wave-length side of the origin, and to the band heads due to $Rb^{85}Rb^{87}$ at the long wave-length side of the origin.

Equations to represent the frequencies of the assigned bands have been found by a method of least squares. The equation

$$\nu = 14{,}662.6 + 48.05(v' + \tfrac{1}{2}) - 0.191(v' + \tfrac{1}{2})^2 - \left[57.31(v'' + \tfrac{1}{2}) - 0.105(v'' + \tfrac{1}{2})^2\right] \qquad (6)$$

has been found to represent adequately the frequencies of the bands attributed to the molecule $Rb^{85}Rb^{85}$. The equation

$$\nu = 14{,}662.6 + 47.78(v' + \tfrac{1}{2}) - 0.188(v' + \tfrac{1}{2})^2 - \left[56.98(v'' + \tfrac{1}{2}) - 0.103(v'' + \tfrac{1}{2})^2\right] \qquad (7)$$

then applies to bands attributed to the molecule $Rb^{85}Rb^{87}$ and has been obtained from the first equation by multiplying the constants by suitable powers of ρ ($\rho = 0.9943$). The quantum numbers, the measured frequencies, estimated intensities and the differences between the observed values and those calculated from Eqs. (6) and (7) are given in Table VII. Due to a slightly misplaced comparison spectrum the values given in Table VII may be in error by a small constant amount, but these errors probably lie well within the error of measurement. A great many of the observed band heads have also been measured in absorption on a 21-ft. grating. The positions of these band heads agree essentially with those observed in magnetic rotation and are not recorded except in the few cases where a band head

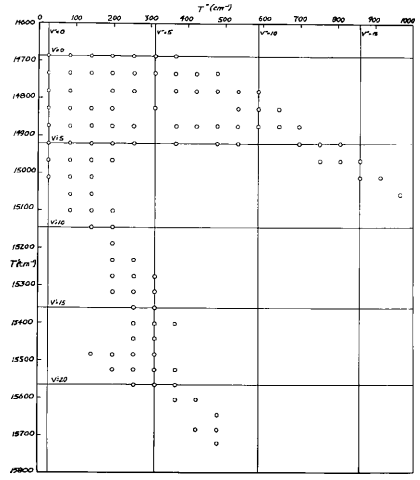

Fig. 6. Franck-Condon diagram for the $^1\Pi \leftarrow {}^1\Sigma$ system of Rb_2.

was observed in absorption only. Intensities are given both for magnetic rotation and absorption, and where an intensity is given for absorption only, the frequency is that observed in absorption.

A Franck-Condon diagram for this system is given in Fig. 6. Since the system studied lies on the violet side of the resonance doublet of the Rb atom, and since the magnetic rotation lines correlate immediately with the absorption

TABLE VII. Band heads of rubidium observed in magnetic rotation.

i MAG. ROT.	i ABS.	ν OBSERVED	v'	v''	$\nu_{obs.} - \nu_{calc.}$
	3	15358.6			
	3	15341.0	2	18	-2.6
	3	15322.7	3	19	-5.0
3	3	15305.5	4	20	-6.1
3	4	15288.1	3	18	+1.2
1	4	15268.9	4	19	-2.3
2		15262.6	7	23	+0.2
4	4	15252.7	5	20	-2.7
3		15245.6	8	24	0.0
	4	15232.0	4	18	+1.6
2		15238.2	6	21	-1.2
4	3	15215.9	5	19	+0.9
2		15207.0	8	23	-0.7
4	3	15200.9	6	20	+1.6
4	3	15190.6	4	17	+1.4
4	3	15183.2	7	21	-0.3
5	2	15176.0	5	18	+1.8
3		15168.3	8	22	+0.9
7	4	15160.8	6	19	+1.9
6	3	15147.7	4	16	+0.1
6	3	15134.3	5	17	+1.3
8	3	15119.9	3	14	0.0
8	3	15107.2	4	15	+1.5
8	3	15093.4	5	16	+2.0
9	3	15078.1	3	13	+0.9
8	3	15064.2	4	14	+0.8
7	3	15050.3	5	15	+0.8
5		15038.7	6	16	+3.4

i MAG. ROT.	i ABS.	ν OBSERVED	v'	v"	$\nu_{obs.} - \nu_{calc.}$
6	3	15032.8	3	12	-1.3
7	4	15021.9	4	13	+1.2
7		15016.3	1	9	+0.2
7		15008.4	5	14	+1.2
7	3	15002.6	2	10	-0.9
8	4	14989.8	3	11	-0.8
4		14983.8	0	7	+0.2
6		14977.8	4	12	+0.2
7		14970.3	1	8	-1.2
3		14964.3	5	13	-0.2
8	3	14958.7	2	9	-0.5
8		14945.6	3	10	-1.2
4	4	14936.9	0	6	-1.4
10	5	14925.7	1	7	-0.8
7	6	14913.9	2	8	-0.7
4		14902.5	3	9	0.0
10	6	14892.0	0	5	-0.5
10	5	14881.0	1	6	-0.2
3		14868.9	2	7	-0.7
2		14853.5			
10	10	14846.8	0	4	+0.4
6	5	14835.3	1	5	-0.1
5	3	14822.3	2	6	-2.0
4		14815.5			
3		14808.0			
12	10	14800.9	0	3	+1.1
4	4	14790.3	1	4	+1.0
5		14778.8	2	5	+0.3
4		14766.6	3	6	-1.0

i MAG. ROT.	i ABS.	ν OBSERVED	v'	v"	$\nu_{obs.} - \nu_{calc.}$
8	10	14754.5	0	2	+1.6
2		14746.7	1	3	+4.0
5	7	14732.7	2	4	+0.3
5		14727.5			
6	4	14720.6	3	5	-1.2
8	10	14706.5	0	1	+0.8
7		14697.7	1	2	+1.9
7	5	14685.3	2	3	-0.5
3		14676.0	3	4	+0.3
2		14665.6	4	5	+0.3
4	4	14660.2	0	0	+2.3
9	10	14649.7	1	1	+1.0
3		14629.2	3	3	-0.1
4	5	14618.7	4	4	-0.8
6	8	14603.4	1	0	+2.2
	6	14593.0	2	1	+0.9
7	5	14582.8	3	2	+0.1
1		14551.7	6	5	-2.0
8	10	14545.9	2	0	+1.3
3		14538.9	3	1	+3.2
5	5	14527.1	4	2	+0.5
5	3	14515.6	5	3	-1.6
3		14508.6	6	4	+0.8
10	10	14489.3	3	0	+1.1
3	3	14483.0	4	1	+3.4
4		14464.8			
5		14450.3	7	4	-1.9
2		14441.6	8	5	-1.2
8	10	14432.4	4	0	+0.3

i MAG. ROT.	i ABS.	ν OBSERVED	v'	v"	$\nu_{obs.} - \nu_{calc.}$
8	4	14422.7	5	1	-0.9
4	3	14414.2	6	2	-0.7
	2	14395.9	8	4	-1.0
3	8	14386.3	9	5	-1.4
6	4	14376.0	5	0	-0.1
8	4	14367.1	6	1	-0.8
5	3	14358.5	7	2	-0.8
	3	14343.3	9	4	+1.5
1	4	14320.6	6	0	+0.2
3	3	14312.2	7	1	-0.1
4	3	14303.1	8	2	-0.9
3	2	14294.4	9	3	-1.1
1		14285.2	10	4	-1.7
1		14256.7	8	1	-0.3
4		14248.5	9	2	-0.4
5		14239.3	10	3	-1.3
5		14231.4	11	4	-0.7
4		14223.4	12	5	-0.1
1		14214.0	13	6	-0.7
2		14193.5	10	2	-0.5
3		14184.8	11	3	-1.0
3		14176.4	12	4	-1.2
3		14168.4	13	5	-0.8
2		14160.0	14	6	-0.6
1		14153.4	15	7	+1.4
1		14115.6	14	5	+0.5
1		14108.4	15	6	+1.6
1		14099.8	16	7	+1.5
1		14092.0	17	8	+2.4

heads, one may conclude, by analogy with Li_2 and Na_2, that the transition is $^1\Pi \leftarrow {}^1\Sigma$.

Extrapolation to dissociation of the upper state of the system according to Eq. (6) yields 17,685 cm^{-1} as the energy of dissociation of the upper state. The upper state dissociates into a normal ^2S atom and one in the ^2P state, but it is not known whether this atom is in the $^2P_{\frac{1}{2}}$ or $^2P_{3/2}$ state. The ground state dissociates into two normal atoms. If the product of dissociation of the upper state is a $^2P_{\frac{1}{2}}$ atom the energy of dissociation of the lower state becomes 5100 cm^{-1}, and if it is a $^2P_{3/2}$ atom the energy of dissociation becomes 4870 cm^{-1}. Direct extrapolation to dissociation of the lower state yields 7820 cm^{-1} as its energy of dissociation. Since the upper state could be followed nearer to dissociation extrapolation of the upper state probably yields a better value. The energy of dissociation of rubidium has been calculated to be 0.47 volt (3800 cm^{-1}) by interpolation between the known energies of dissociation of potassium and caesium. Experience with the other alkali metals has shown that the energy of dissociation obtained by direct extrapolation is usually too high, so that the value, 5100 cm^{-1}, is probably an upper limit to the energy of dissociation of Rb_2. Since the energies of dissociation of K_2 and Cs_2 are known to a high degree of accuracy the value, 0.47 volt, obtained by interpolation between the known energies of dissociation of K_2 and Cs_2 is still the most reliable value of the energy of dissociation of Rb_2.

5. Other Alkali Metal Molecules.

Due to the method of preparing rubidium which was used, sodium was present as a rather important impurity. Consequently, the new band system in the region 5990-6336 A which occured on the plates of the magnetic rotation spectrum of Rb_2, is attributed to NaRb. It is true that three bands of this system at 16,513 cm^{-1}, 16,571 cm^{-1} and 16,684 cm^{-1} were reported by Walter and Barratt[4] and attributed to Rb_2, but the vibrational intervals in this system confirm my conclusion, for firstly, the ground interval, 107 cm^{-1}, agrees well enough with the

ground interval of a system in the blue green, attributed to NaRb by Walter and Barratt, and analysed by Weizel and Kulp[14], and secondly the vibrational intervals are approximately those which are obtained by interpolation between the known intervals of Na_2 and Rb_2. Moreover since the new band system was observed in magnetic rotation it is due to a $^1\Pi \leftarrow {}^1\Sigma$ transition. By comparing the vibrational frequencies of 107 cm^{-1} and 61 cm^{-1} in the $^1\Sigma$ and $^1\Pi$ states of this molecule with the corresponding vibrational frequencies of the alkali metal molecules given in Table VIII, it is evident that the new band system is not due to any of the alkali metal molecules composed of similar atoms. All of the possible intermetallic compounds may be excluded which do not have one atom of rubidium. Then since the vibrational frequencies of a molecule composed of a rubidium atom and an atom of some other alkali, may be expected to lie between the vibrational frequencies of Rb_2 and those of the molecule composed of two atoms of the other alkali, the new band system could be due only to NaRb and LiRb. But since Li was not observed as an impurity in any of the observations, the molecule is almost certainly NaRb.

Table VIII.

Vibrational intervals in the $^1\Sigma$ and $^1\Pi$ states for the alkali metals.

	$^1\Sigma$	$^1\Pi$
Li_2	351.6	269.7
Na_2	159.2	123.8
K_2	92.6	75.0
Rb_2	57.3	48.1
Cs_2	42.0	34.?

The formula

$$\nu = 16{,}421.8 + 61.49(v' + \tfrac{1}{2}) - 0.945(v' + \tfrac{1}{2})^2 - [106.64(v'' + \tfrac{1}{2}) - 0.455(v'' + \tfrac{1}{2})^2] \qquad (8)$$

was found to represent accurately the frequencies of the observed band heads. The observed frequencies, intensities, assigned quantum numbers and the differences between the observed frequencies and those calculated from Eq. (3) are given in Table IX. A Franck-Condon diagram is given in Fig. 7 and is seen to be normal.

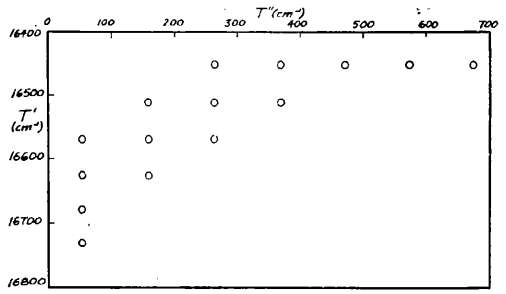

Fig. 7. Franck-Condon diagram for the $^1\Pi \leftarrow {}^1\Sigma$ system of NaRb.

Table IX.

Band heads of NaRb observed in magnetic rotation.

i	ν OBSERVED	v'	v''	$\nu_{obs.} - \nu_{calc.}$	i	ν OBSERVED	v'	v''	$\nu_{obs.} - \nu_{calc.}$
3	16678.3	5	0	+0.1	5	16248.1	1	2	0.0
3	16625.4	4	0	-0.8	2	16189.7	0	2	+1.2
3	16572.2	3	0	0.0	4	16143.5	1	3	-0.7
3	16517.4	2	0	+1.0	4	16083.1	0	3	-1.5
3	16466.9	3	1	+0.4	4	15982.3	0	4	+0.6
5	16410.6	2	1	-0.1	3	15879.7	0	5	+0.2
5	16351.7	1	1	-1.3	3	15778.1	0	6	-0.3
2	16305.8	2	2	0.0					

A system between 7230-7400 A occurs both on the caesium and on the rubidium absorption plates. This system has been found by Matuyama[6] and attributed

to Cs_2. However, the vibrational intervals do not correspond to any known intervals in Cs_2. Neither do they correspond to any known intervals in Rb_2. But the observed intervals of 49.4 cm^{-1} and 38.3 cm^{-1} do fit nicely with intervals for RbCs estimated by interpolation between known intervals for Rb_2 and Cs_2. Since Cs is known to be present as an impurity in the Rb, and vice versa, it seems safe to attribute this system to RbCs.

The band heads in this system may be represented by the formula

$$\nu = 13,747.21 + 38.46(v' + \tfrac{1}{2}) - 49.41(v'' + \tfrac{1}{2}). \qquad (9)$$

The measured frequencies of the bands, together with the differences between the observed frequencies and those calculated from Eq. (9) are given in Table X.

Table X.

Band heads in the system of RbCs at 7200 A.

ν observed	n''	n'	$\nu_{obs.} - \nu_{calc.}$	ν observed	n''	n'	$\nu_{obs.} - \nu_{calc.}$
13818.29	0	2	-0.37	13681.57	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

V. SUMMARY OF RESULTS.

Measurements of four distinct band systems of Cs_2 have been made, in absorption with high and low dispersion, in magnetic rotation and in fluorescence. A complete vibrational analysis of the system at 7667 A has been made. An extrapolation yields 0.45 volt as the energy of dissociation of the ground state. The other systems have not been completely analyzed, though many regularities have been found.

The $^1\Pi \leftarrow {}^1\Sigma$ system of Rb_2 has been observed in magnetic rotation and in absorption. A vibrational analysis has been made, but has not been extended far enough to obtain a reliable value of the energy of dissociation by extrapolation. A fairly reliable value of the energy of dissociation is, however, obtained by interpolation between the known energies of dissociation of the other alkali metal molecules.

A system at 7200 A, previously attributed by some authors to Cs_2, has been observed and attributed to RbCs.

A new system between 5990-6336 A has been observed in magnetic rotation and attributed to NaRb.

VI. ACKNOWLEDGEMENT.

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VII. BIBLIOGRAPHY.

1. Loomis and Nusbaum, Phys. Rev. 38, 1447 (1931)
2. Loomis and Nusbaum, Phys. Rev. 39, 89 (1932)
3. Loomis and Nusbaum, Phys. Rev. 40, 380 (1932)
4. Walter and Barratt, Proc. Roy. Soc., A119, 257 (1928)
5. Rompe, Zeits. f. Physik 74, 175 (1932)
6. Matuyama, Tohoku Imp. Univ. Sci. Rep. 23, 322 (1934)
7. Matuyama, Tohoku Imp. Univ. Sci. Rep. 23, 308 (1934)
8. Wood, Phil. Mag. 6 35, 235 (1918)
9. Kuhn, Zeits. f. Physik 76, 782 (1932)
10. Loomis and Nile, Phys. Rev. 32, 873 (1928)
11. Freudenberg, Zeits. f. Physik 67, 417 (1931)
12. Minkowski and Mühlenbruch, Zeits. f. Physik 63, 198 (1930)
13. Boeckner and Mohler, Bur. Standards J. Research 5, 831 (1930)
14. Weizel and Kulp, Ann. d. Physik 5 4, 971 (1930)