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

i	ν obs	n'	v''	$\nu_{obs}-\nu_{calc}$	i	ν obs	n'	v''	$\nu_{obs}-\nu_{calc}$
2	16054.05	5	6	−0.39	5	15890.70	8	12	−0.14
2	16029.17	1	4	−0.16	7	15878.13	6	11	−0.23
1	16027.87	4	6	+0.03	3	15877.33	9	13	+0.29
3	16025.26	7	8	−0.44	9	15864.49	7	12	−0.19
2	16015.43	2	5	+0.24	5	15851.60	5	11	−0.30
4	16013.27	5	7	−0.33	7	15850.82	8	13	−0.20
4	16011.81	8	9	−0.46	8	15837.47	9	12	+0.09
4	16001.78	0	4	−0.35	10	15824.70	7	13	−0.15
2	16000.47	3	6	−0.61	3	15824.05	10	15	+0.26
4	15999.03	6	8	−0.35	4	15811.85	5	12	−0.05
5	15988.30	1	5	+0.15	6	15811.06	8	14	−0.30
4	15986.82	4	7	−0.18	5	15797.92	9	15	+0.01
3	15985.01	7	9	−0.18	4	15785.21	7	14	+0.01
1	15974.73	2	6	+0.55	4	15784.50	10	16	+0.02
4	15972.56	5	8	−0.36	9	15771.83	5	13	−0.25
8	15971.19	8	10	+0.18			8	15	−0.06
5	15960.55	0	5	−0.40	6	15758.96	6	14	+0.08
		3	7	+0.31	7	15758.54	9	16	−0.04
6	15946.98	1	6	−0.16	6	15745.44	7	15	−0.29
7	15946.33	4	8	+0.01			10	17	+0.08
4	15945.01	7	10	+0.16	8	15732.42	8	16	−0.15
9	15932.13	5	9	−0.28	7	15719.45	9	17	−0.03
4	15930.82	8	11	−0.02	6	15706.45	10	18	+0.04
1	15919.24	3	8	−0.32	4	15693.40	8	17	−0.06
5	15918.18	6	10	−0.35	6	15680.52	9	18	−0.01
0	15905.99	4	9	+0.19	5	15667.79	10	19	+0.15
4	15904.46	7	11	−0.22	4	15654.75	11	20	−0.03
4	15892.00	5	10	−0.07	4	15641.78	9	19	+0.02
					4	15629.31	10	20	+0.26

tified with ours, 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

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

v'' is the true quantum number, and n' differs from the true v' by some unknown constant. The ground state is identical to the one previously reported.[1] The observed band heads, their intensities, assignments and the differences between the observed values and those given by Eq. (1) are given in Table I.

The bands in this system, degraded to the blue, and previously reported may be represented by the formula

$$\nu = 16{,}066.03 + 29.38(n'+\tfrac{1}{2}) - 0.0796(n'+\tfrac{1}{2})^2 - [41.990(v''+\tfrac{1}{2}) - 0.080051(v''+\tfrac{1}{2})^2 - 0.000164266(v''+\tfrac{1}{2})^3]. \quad (2)$$

The formula previously reported[1] contained an error.

This band system is extraordinarily complex and a great many observed features have not been explained, even though the two systems, degraded to the red and to the blue, do include the more obvious features of the system.

FEBRUARY 1, 1936 PHYSICAL REVIEW VOLUME 49

The Band Spectra of Rubidium and of Its Combinations with Other Alkali Metals

P. KUSCH, *University of Illinois*

(Received December 5, 1935)

The magnetic rotation spectrum of Rb_2 has been observed and a vibrational analysis made. The vibrational frequency in the $^1\Sigma$ ground state is 57.31 cm^{-1} and that in the excited $^1\Pi$ state, 48.05 cm^{-1}. The magnetic rotation spectrum of NaRb has also been found and has the vibrational frequencies 106.6 cm^{-1} and 61.5 cm^{-1} in the $^1\Sigma$ ground and excited $^1\Pi$ states, respectively. A band system due to RbCs has been identified.

THE purpose of this investigation is to extend our knowledge of the band spectra of the alkali metals to Rb_2, the only one of the group not previously investigated by means of accurate methods. Rather complete vibrational analyses have been made[1] of the spectra of Li_2, Na_2 and K_2, and their energies of dissociation determined by means of their magnetic rotation spectra.

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

The absorption spectrum of Cs_2 has been investigated[2] and an accurate value of its energy of dissociation found. Matuyama[3] has reported an analysis of the spectrum of Rb_2 under low dispersion but has not found a value of the energy of dissociation.

In the present investigation the magnetic rotation spectrum and the absorption spectrum of Rb_2 in the region 6500–7100A 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.

The same apparatus was used for the observation of the magnetic rotation spectrum that Loomis and Nusbaum[1a] used for their investigations of the other alkali metals. The nickel tube which they used was replaced by a glass tube to which windows had been fused. The ends of the tube were carefully annealed to relieve the strains introduced in the windows by the process of fusing the windows to the tube. 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 in the absence of a magnetic field.

Rubidium, prepared by heating dry rubidium chloride with metallic calcium, in vacuum, was distilled into the system. Temperatures and vapor pressures corresponding to temperatures of about 320°C could be applied to the tube for long intervals of time without appreciably blackening the tube. At higher temperatures the inside of the tube quickly blackened and became opaque. The impossibility of working with higher pressures of rubidium with this technique accounts for the difficulty of extending the band system to very high quantum numbers.

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

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

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

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

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. (1) and (2) are given in Table I. Due to a slightly misplaced comparison spectrum the values given in Table I 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

[2] Loomis and Kusch, Phys. Rev. **46**, 292 (1934).
[3] Matuyama, Tohoku Imp. Univ. Sci. Rep. **23**, 308 (1934).

TABLE I. *Band heads of rubidium observed in magnetic rotation.*

i Mag. Rot.	i Abs.	ν Observed	v'	v''	νobs $-\nu$calc	i Mag. Rot.	i Abs.	ν Observed	v'	v''	νobs $-\nu$calc	i Mag. Rot.	i Abs.	ν Observed	v'	v''	νobs $-\nu$calc
	3	15358.6				8		14945.6	3	10	−1.2	5	5	14527.1	4	2	+0.5
	3	15341.0	2	18	−2.6	4	4	14936.9	0	6	−1.4	5	3	14515.6	5	3	−1.6
	3	15322.7	3	19	−5.0	10	5	14925.7	1	7	−0.8	3		14508.6	6	4	+0.8
3	3	15305.5	4	20	−6.1	7	6	14913.9	2	8	−0.7	10	10	14489.3	3	0	+1.1
3	4	15288.1	3	18	+1.2	4		14902.5	3	9	0.0	3	3	14483.0	4	1	+3.4
1	4	15268.9	4	19	−2.3	10	6	14892.0	0	5	−0.5	4		14464.8			
2		15262.6	7	23	+0.2	10	5	14881.0	1	6	−0.2	5		14450.3	7	4	−1.9
4	4	15252.7	5	20	−2.7	3		14868.9	2	7	−0.7	2		14441.6	8	5	−1.2
3		15245.6	8	24	0.0	2		14853.5				8	10	14432.4	4	0	+0.3
	4	15232.0	4	18	+1.6	10	10	14846.8	0	4	+0.4	8	4	14422.7	5	1	−0.9
2		15238.2	6	21	−1.2	6	5	14835.3	1	5	−0.1	4	3	14414.2	6	2	−0.7
4	3	15215.9	5	19	+0.9	5	3	14822.3	2	6	−2.0		2	14395.9	8	4	−1.0
2		15207.0	8	23	−0.7	4		14815.5				3	8	14386.3	9	5	−1.4
4	3	15200.9	6	20	+1.6	3		14808.0				6	4	14376.0	5	0	−0.1
4	3	15190.6	4	17	+1.4	12	10	14800.9	0	3	+1.1	8	4	14367.1	6	1	−0.8
4	3	15183.2	7	21	−0.3	4	4	14790.3	1	4	+1.0	5	3	14358.5	7	2	−0.8
5	2	15176.0	5	18	+1.8	5		14778.8	2	5	+0.3		3	14343.3	9	4	+1.5
3		15168.3	8	22	+0.9	4		14766.6	3	6	−1.0	1	4	14320.6	6	0	+0.2
7	4	15160.8	6	19	+1.9	8	10	14754.5	0	2	+1.6	3	3	14312.2	7	1	−0.1
6	3	15147.7	4	16	+0.1	2		14746.7	1	3	+4.0	4	3	14303.1	8	2	−0.9
6	3	15134.3	5	17	+1.3	5	7	14732.7	2	4	+0.3	3	2	14294.4	9	3	−1.1
8	3	15119.9	3	14	0.0	5		14727.5				1		14285.2	10	4	−1.7
8	3	15107.2	4	15	+1.5	6	4	14720.6	3	5	−1.2	1		14256.7	8	1	−0.3
8	3	15093.4	5	16	+2.0	8	10	14706.5	0	1	+0.8	4		14248.5	9	2	−0.4
9	3	15078.1	3	13	+0.9	7		14697.7	1	2	+1.9	5		14239.3	10	3	−1.3
8	3	15064.2	4	14	+0.8	7	5	14685.3	2	3	−0.5	5		14231.4	11	4	−0.7
7	3	15050.3	5	15	+0.8	3		14676.0	3	4	+0.3	4		14223.4	12	5	−0.1
5		15038.7	6	16	+3.4	2		14665.6	4	5	+0.3	1		14214.0	13	6	−0.7
6	3	15032.8	3	12	−1.3	4	4	14660.2	0	0	+2.3	2		14193.5	10	2	−0.5
7	4	15021.9	4	13	+1.2	9	10	14649.7	1	1	+1.0	3		14184.8	11	3	−1.0
7		15016.3	1	9	+0.2	3		14629.2	3	3	−0.1	3		14176.4	12	4	−1.2
7		15008.4	5	14	+1.2	4	5	14618.7	4	4	−0.8	3		14168.4	13	5	−0.8
7	3	15002.6	2	10	−0.9	6	8	14603.4	1	0	+2.2	2		14160.0	14	6	−0.6
8	4	14989.8	3	11	−0.8		5	14593.0	2	1	+0.9	1		14153.4	15	7	+1.4
4		14983.8	0	7	+0.2	7	5	14582.8	3	2	+0.1	1		14115.6	14	5	+0.5
6		14977.8	4	12	+0.2	1		14551.7	6	5	−2.0	1		14108.4	15	6	+1.6
7		14970.3	1	8	−1.2	8	10	14545.9	2	0	+1.3	1		14099.8	16	7	+1.5
3		14964.3	5	13	−0.2	3		14538.9	3	1	+3.2	1		14092.0	17	8	+2.4
8	3	14958.7	2	9	−0.5												

head 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. 1. 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 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. (1) 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 $^2P_{1/2}$ or $^2P_{3/2}$ state. The ground state dissociates into two normal atoms. If the product of dissociation of the upper state is a $^2P_{1/2}$ 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[2] 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

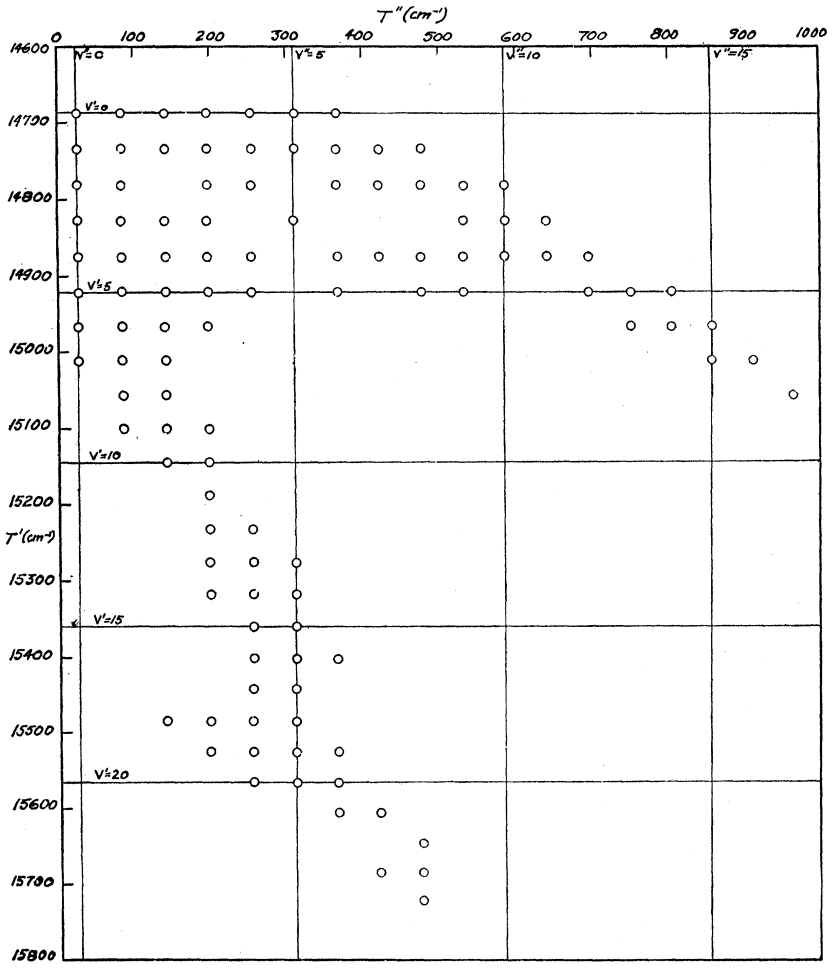

FIG. 1. Franck-Condon diagram for the $^1\Pi \leftarrow {}^1\Sigma$ system of Rb_2.

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.

Due to the method of preparing rubidium which was used, sodium was present as a rather important impurity. Consequently we attribute to NaRb the new band system which occurred on our plates in the region 5990–6336A. 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 our conclusion, for firstly, the ground interval, 107 cm^{-1}, agrees well enough with one which is prominent in the green system which Walter and Barratt do attribute to NaRb; 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 II, 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 com-

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

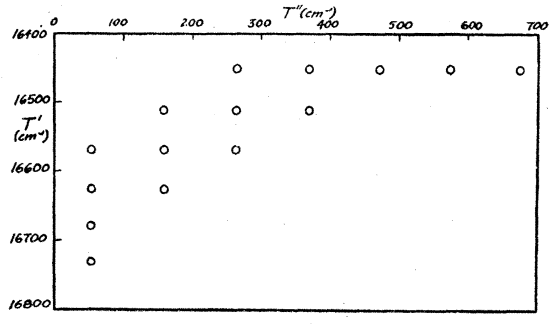

FIG. 2. Franck-Condon diagram for the $^1\Pi \leftarrow {}^1\Sigma$ system of NaRb.

pounds 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.

The formula

$$\nu = 16{,}421.8 + 61.49(v'+\tfrac{1}{2}) - 0.945(v'+\tfrac{1}{2})^2 - [106.64(v''+\tfrac{1}{2}) - 0.455(v''+\tfrac{1}{2})^2] \quad (3)$$

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 III. A Franck-Condon diagram is given in Fig. 2 and is seen to be normal.

The system between 7230–7400A which was found by Loomis and Kusch[2] in caesium absorption also occurs on our rubidium absorption plates. This system has also been found by Matuyama[5] and attributed to Cs_2. However, as Loomis and Kusch pointed out, 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. Although the progressions in this system are not long enough to fix the vibrational assignments uniquely, nevertheless the assignments given by Loomis and Kusch are very plausible, since, in addition to yielding vibrational intervals, which, on the above view are entirely reasonable, they also lead to a normal Franck-Condon diagram, which Matuyama's assignments do not. The arbitrary numbers previously assigned to the bands are undoubtedly the true quantum numbers v' and v''.

TABLE II. *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	34.2

TABLE III. *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					

The band heads in this system are then given by the formula

$$\nu = 13{,}747.21 + 38.46(v'+\tfrac{1}{2}) - 49.41(v''+\tfrac{1}{2}). \quad (4)$$

The data given by Matuyama are more extensive than those given by Loomis and Kusch.

The author wishes to express his appreciation to Professor F. W. Loomis for his interest and helpful suggestions.

[5] Matuyama, Tohoku, Imp. Univ. Sci. Rep. **23**, 322 (1934).