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Band Spectra and Energy of Dissociation of the Rubidium Molecule

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Measurements and vibrational analysis of the violet and blue band systems of Rb_2 have been made in absorption. Quantum numbers have been assigned to 118 and 160 bands in the two systems, respectively. The upper vibrational frequency of the violet system is 40.42 cm^{-1} and that of the blue one, 36.46 cm^{-1}. The lower level, common to the two systems, is $^1\Sigma$ ground state, and its vibrational frequency is found to be 57.45 cm^{-1}. The energies of dissociation of the three states of the molecule have been determined by means of extrapolation, and the value for the ground state is 0.49 ± 0.02 volt. A green edge of the blue system at 5032A has been observed.

INTRODUCTION

THE band spectra of Rb_2 have been observed by Carter,[1] Bevan,[2] Dunoyer,[3] McLennan and Ainslie,[4] and Walter and Barratt[5] with instruments of low dispersion. Matuyama[6] has studied the bands in absorption and classified them into four systems. Two systems in the red and infrared regions, associated with the doublet of the first member of the principal series, have been found to be due to the transitions of $^1\Pi \leftarrow {}^1\Sigma$ and $^1\Sigma \leftarrow {}^1\Sigma$, respectively. The other two systems in the blue and violet regions, on the longer wave-length side of the second member of the principal series, appeared only in a denser vapor. Matuyama has reported an analysis of these systems but has not found a value of the energy of dissociation.

Recently Kusch[7] measured and analyzed the magnetic rotation spectrum and absorption spectrum in the region 6500–7100A with instrument of high dispersion, but the data were still not extensive enough for the determination of an accurate value of energy of dissociation.

The purpose of this investigation is to obtain a complete analysis of the violet and blue systems of Rb_2 and to extend the band systems to high quantum numbers in order to yield a reliable value of the energy of dissociation.

EXPERIMENTAL

A steel absorption tube, 120 cm long, 3 cm internal diameter, was used with quartz windows at the ends. The tube was electrically heated on the main part and cooled near the ends by a circulation of water. In order to prevent quick distillation of the metallic vapor, the tube was filled with nitrogen at 4 cm Hg pressure at room temperature. The introduction of the gas had not affected the absorption spectra materially. The metal was prepared by reducing rubidium chloride with metallic calcium. The temperature of the absorbing vapor in our experiments varied from 350°C to 400°C, as measured by a steel-constantan thermocouple. An incandescent lamp was used as a source of continuous spectrum. The spectrograms were taken in the second-order spectrum with a 3 m concave grating of Eagle mounting, the dispersion of which was about 2.8A/mm. An iron arc was taken as the comparison spectrum.

RESULTS

A. The violet system

At about 350°C, the band system begins to appear, having its maximum intensity at 4300A. With increasing temperature, this system spreads out in both directions. On the short wave-length side it approaches rapidly to the 4202 and 4216A doublet. On the long wave-length side it terminates, gradually with decreasing intensity, at the doublet 4555 and 4593A of caesium which appeared as impurity. All band heads are rather sharp, and the bands are degraded to the red. The rotational structure can be seen on the plate

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[1] Carter, Physik. Zeits. **11**, 632 (1910).

[2] Bevan, Proc. Roy. Soc. London **85**, 61 (1911).

[3] Dunoyer, Le Rad. **9**, 218 (1912).

[4] McLennan and Ainslie, Proc. Roy. Soc. London **103**, 304 (1923).

[5] Walter and Barratt, Proc. Roy. Soc. London **119**, 257 (1928).

[6] Matuyama, Tohoku Imp. Univ. Sci. Rep. **23**, 308 (1934).

[7] Kusch, Phys. Rev. **49**, 218 (1936).

but it is not sufficiently resolved to be measured. We have measured 118 band heads in the system and assigned vibrational quantum numbers to all of them.

The frequencies of the bands can be represented by the following equation found by the method of least squares

$$\nu = 22777.5 + [40.42(v'+\tfrac{1}{2}) - 0.0745(v'+\tfrac{1}{2})^2 - 0.00144(v'+\tfrac{1}{2})^3] - [57.45(v''+\tfrac{1}{2}) - 0.104(v''+\tfrac{1}{2})^2]. \quad (1)$$

Since the values of ω_e and $x_e\omega_e$ in the lower state are approximately the same as those of the ground state of the red system (57.31 and 0.105) obtained by Kusch,[7] the lower state of the system is therefore the $^1\Sigma$ ground state.

The measured frequencies ($\nu_{\text{obs.}}$), the estimated intensities (I), the assigned quantum numbers (v', v'') and the differences ($\Delta\nu$) between the measured frequencies and those calculated from the Eq. (1) are given in Table I. The average value of $|\Delta\nu|$ is 0.68 cm^{-1}.

An improved Franck-Condon[8] diagram for the system is shown in Fig. 1. The diagram appears to be normal.

B. The blue system

This band system begins to appear at 360°C, a temperature a little higher than that for the violet system, having its maximum intensity at 4750A. With increasing temperature the system extends out in both directions, slowly toward the red and rapidly toward the violet. On the short wave-length side it approaches to 4700A with apparently decreasing intensity. On the long

TABLE I. *Band heads in the violet system of Rb_2.*

ν observed	I	v'	v''	$\Delta\nu$ $\nu_{\text{obs.}}-\nu_{\text{cal.}}$	ν observed	I	v'	v''	$\Delta\nu$ $\nu_{\text{obs.}}-\nu_{\text{cal.}}$	ν observed	I	v'	v''	$\Delta\nu$ $\nu_{\text{obs.}}-\nu_{\text{cal.}}$
23673.3	3	24	0	+0.1	23008.7	6	6	0	+0.7	22565.7	5	2	5	+0.4
23649.3	3	25	1	−0.6	22989.9	6	7	1	0.0	22549.8	3	3	6	+0.8
23638.9	4	23	0	+0.1	22972.1	8	8	2	+0.3	22533.2	2	4	7	+0.5
23615.9	4	24	1	−0.1	22969.3	4	5	0	+0.7	22525.6	2	1	5	+0.4
23604.2	5	22	0	+0.1	22953.9	3	9	3	+0.2	22509.2	4	2	6	+0.1
23581.9	5	23	1	+0.3	22950.9	4	6	1	+0.1	22501.7	3	6	9	+1.4
23569.0	5	21	0	0.0	22934.6	4	10	4	−1.0	22494.4	2	3	7	+1.4
23547.5	5	22	1	+0.6	22933.0	8	7	2	+0.2	22484.9	1	0	5	0.0
23533.4	6	20	0	−0.3	22929.3	5	4	0	+0.3	22468.9	4	1	6	−0.1
23512.3	5	21	1	+0.5	22915.3	3	8	3	+0.3	22453.7	3	2	7	+0.6
23497.4	7	19	0	−0.6	22893.7	7	6	2	0.0	22446.6	2	6	10	+1.7
23476.4	5	20	1	−0.1	22876.2	4	7	3	+0.3	22437.3	2	3	8	+0.1
23461.4	7	18	0	−0.5	22872.1	3	4	1	+0.3	22428.5	1	0	6	−0.2
23440.2	5	19	1	−0.6	22854.9	5	5	2	+0.6	22412.8	3	1	7	−0.2
23425.0	7	17	0	−0.6	22837.0	7	6	3	+0.1	22397.7	2	2	8	+0.4
23403.8	5	18	1	−0.9	22815.0	3	4	2	+0.3	22380.9	2	3	9	−0.7
23388.3	8	16	0	−0.7	22802.3	3	8	5	+0.3	22371.8	2	0	7	−0.9
23367.3	6	17	1	−1.1	22797.9	6	5	3	+0.4	22357.1	3	1	8	−0.1
23363.8	3	20	3	+1.2	22792.7	4	2	1	+0.5	22342.2	2	2	9	+0.5
23351.1	9	15	0	−0.9	22783.6	2	9	6	−0.9	22326.5	1	3	10	+0.3
23330.3	6	16	1	−1.5	22775.7	3	3	2	+0.7	22316.0	2	0	8	−0.9
23313.5	10	14	0	−1.3	22769.6	3	0	0	+0.6	22302.1	3	1	9	+0.5
23293.2	6	15	1	−1.6	22758.6	6	4	3	+0.7	22286.3	2	2	10	0.0
23275.5	9	13	0	−1.8	22735.6	4	2	2	+0.5	22261.2	2	0	9	−0.1
23255.7	6	14	1	−1.9	22719.0	3	3	3	+0.8	22246.3	2	1	10	+0.1
23255.1	4	17	3	+0.6	22712.1	2	0	1	+0.3	22231.3	1	2	11	+0.1
23237.7	9	12	0	−1.9	22702.4	5	4	4	+1.1	22215.8	1	3	12	−1.3
23218.4	6	13	1	−1.7	22695.8	4	1	2	+0.8	22206.1	2	0	10	+0.2
23199.9	9	11	0	−1.7	22678.6	3	2	3	+0.3	22191.3	1	1	11	+0.2
23181.1	7	12	1	−1.3	22670.0	2	6	6	+2.3	22176.2	1	2	12	−1.0
23161.9	6	10	0	−1.4	22662.6	5	3	4	+1.0	22150.8	2	0	11	0.0
23145.6	4	14	3	+1.9	22652.7	4	7	7	+1.9	22136.0	1	1	12	−1.1
23143.5	9	11	1	−0.9	22646.2	3	4	5	+1.3	22121.1	1	2	13	−1.3
23123.5	6	9	0	−1.3	22638.9	3	1	3	+0.7	22095.8	2	0	12	−1.0
23105.5	10	10	1	−0.6	22633.8	2	8	8	−0.2	22081.4	1	1	13	−0.9
23085.0	6	8	0	−1.1	22622.3	2	2	4	+0.6	22067.1	1	2	14	−0.8
23067.6	9	9	1	0.0	22613.2	2	6	7	+1.5	22040.9	1	0	13	−1.1
23047.2	6	7	0	+0.1	22605.4	5	3	5	+0.2	22026.9	1	1	14	−0.9
23029.0	9	8	1	+0.1	22590.2	3	4	6	+1.5					
23010.6	4	9	2	+0.1	22581.8	2	1	4	+0.2					

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[8] Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931).

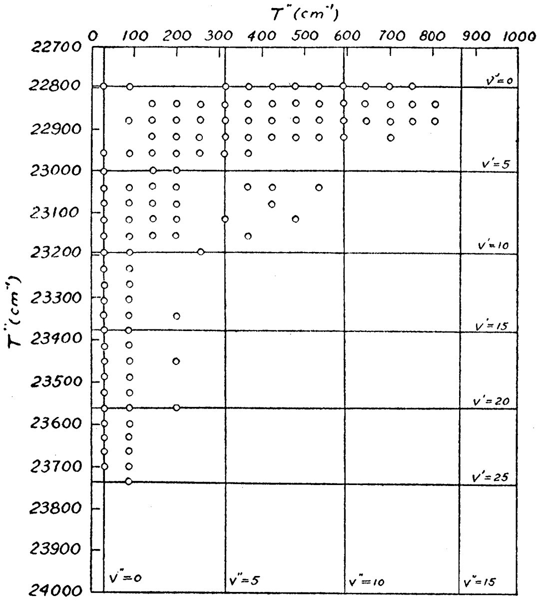

FIG. 1. Improved Franck-Condon diagram for the violet system.

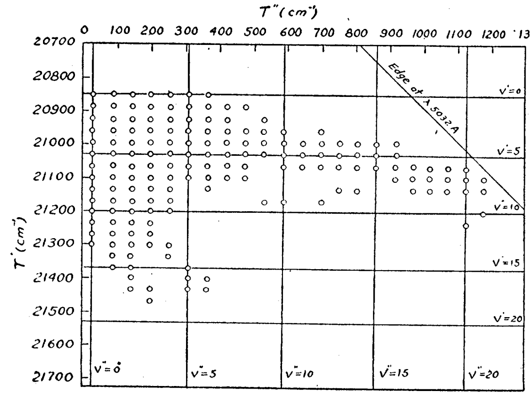

FIG. 2. Improved Franck-Condon diagram for the blue system.

wave-length side it terminates abruptly at higher temperatures (>380°C) in an edge at 5032A, just in the same manner as the 5223A edge of the blue-green band system of Cs_2 reported by Loomis and Kusch.[9]

All band heads in the system, except those in the region of longer wave-length appearing at higher temperatures, are sharp. The bands are degraded to the red. We have measured 167 heads and assigned vibrational quantum numbers to 160 of them.

The frequencies of all assigned bands can be represented by the following equation found by the method of least squares

$$\begin{aligned}\nu = 20835.1 + [&36.46(v'+\tfrac{1}{2}) \\ &-0.124(v'+\tfrac{1}{2})^2] - [56.78(v''+\tfrac{1}{2}) \\ &-0.0785(v''+\tfrac{1}{2})^2 - 0.00083(v''+\tfrac{1}{2})^3]. \quad (2)\end{aligned}$$

In the blue system the lower vibrational quantum numbers extends far to 21. It is hard to represent the lower vibrational terms satisfactorily by a polynomial of second degree as in the case of the violet system. As the vibrational frequencies in Eqs. (1) and (2) are approximately equal, we may therefore conclude that the lower state in the blue system as well as that in the violet system is the $^1\Sigma$ ground state. In the case of K_2, Loomis and Nusbaum[10] have pointed out that the polynomial of low degree could be considered as the best available representation of the constants of the molecule near the equilibrum point, whereas the extrapolation to dissociation could be based on the equation of higher orders. According to this idea, we regard 57.45 cm^{-1} as the lower vibrational frequency and use the constants in Eq. (2) for the determination of energy of dissociation of the ground state.

The measured frequencies ($\nu_{\text{obs.}}$), the estimated intensities (I), the assigned quantum numbers (v', v'') and the difference ($\Delta\nu$) between the measured frequencies and those calculated from Eq. (2) are given in Table II. The unidentified bands are also included. The mean value of $|\Delta\nu|$ is 0.66 cm^{-1}.

The upper and lower vibrational terms of the bands are plotted in Fig. 2, with the green edge at 5032A represented by a straight line on the upright corner. The diagram is also normal. It will be noted that in this case the right arm of the locus is more extensive, while in the violet system, on the contrary, the left is more extensive. The blue system extends the lower vibrational quantum numbers to 21 while the violet system extends the upper vibrational quantum numbers to 25. These two extensions of the vibrational quantum numbers are all favorable for the determination of energy of dissociation.

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[9] Loomis and Kusch, Phys. Rev. **46** 292 (1934).

[10] Loomis and Nusbaum, Phys. Rev. **39**, 89 (1932).

TABLE II. *Band heads in the violet system of* Rb_2.

ν observed	I	v'	v''	$\Delta\nu$ $\nu_{\text{obs.}}-\nu_{\text{cal.}}$	ν observed	I	v'	v''	$\Delta\nu$ $\nu_{\text{obs.}}-\nu_{\text{cal.}}$	ν observed	I	v'	v''	$\Delta\nu$ $\nu_{\text{obs.}}-\nu_{\text{cal.}}$
21293.0	0	17	2	−0.6	20890.1	6	5	2	−0.3	20504.9	5	2	7	+0.5
21284.1	0	15	1	−1.3	20882.2	5	8	4	+0.1	20501.1	4	5	9	+0.8
21275.1	0	13	0	−1.0	20876.8	5	3	1	+0.6	20487.3	3	0	6	−0.4
21268.7	0	18	3	−0.6	20868.7	5	6	3	−0.3	20486.1	6	3	8	+1.4
21260.6	1	16	2	−0.7	20861.4	7	1	0	+0.3	20481.5	5	6	10	+1.3
21250.9	1	14	1	−1.7	20854.7	6	4	2	−0.4	20474.9	5	9	12	−0.4
21242.1	1	12	0	−0.9	20847.6	6	7	4	−0.1	20468.3	4	1	7	−0.1
21236.5	1	17	3	−0.8	20844.6	4				20466.3	6	4	9	+1.3
21227.8	2	15	2	−1.1	20840.0	9	2	1	−0.5	20446.3	5	5	10	+1.0
21218.1	2	13	1	−1.4	20833.7	6	5	3	−0.4	20431.1	5	3	9	+1.5
21208.6	2	11	0	−0.9	20825.2	7	0	0	+0.3	20426.5	4	6	11	+1.1
21195.1	2	14	2	−1.0	20819.2	5	3	2	−0.5	20412.8	3	1	8	−0.2
21185.1	2	12	1	−1.3	20812.6	5	6	4	−0.3	20411.3	6	4	10	+1.3
21175.1	2	10	0	−0.7	20804.3	8	1	1	−0.2	20395.1	4	2	9	+1.2
21162.1	3	13	2	−0.9	20798.5	7	4	3	−0.3	20391.5	5	5	11	+1.0
21152.1	3	11	1	−0.8	20791.7	4	7	5	−0.1	20385.3	4	8	13	−0.5
21141.3	4	9	0	−0.5	20783.2	5	2	2	−0.8	20376.3	5	3	10	+1.7
21128.5	5	12	2	−1.4	20777.6	4	5	4	−0.4	20371.9	3	6	12	+1.0
21124.1	4	17	5	−1.2	20770.2	4	8	6	−0.2	20356.3	5	4	11	+1.1
21118.6	5	10	1	−0.6	20767.8	5	0	1	−0.5	20336.7	5	5	12	+0.7
21107.6	6	8	0	0.0	20763.0	6	3	3	−0.4	20330.7	4	8	14	−1.0
21105.6	4	13	3	−1.1	20756.5	5	6	5	−0.5	20317.6	4	6	13	+1.0
21095.1	8	11	2	−1.3	20747.3	8	1	2	−0.7	20301.6	4	4	12	+0.9
21091.9	5	16	5	−1.1	20742.6	6	4	4	−0.1	20282.4	4	5	13	+0.7
21084.6	6	9	1	−0.6	20736.2	5	7	6	+0.2	20266.4	4	3	12	+1.1
21082.0	5	14	4	−1.7	20727.5	6	2	3	−0.2	20263.2	4	6	14	+0.7
21073.6	7	7	0	+0.4	20721.3	5	5	5	−0.8	20247.1	4	4	13	+0.7
21072.0	5	12	3	−1.6	20711.3	7	0	2	−0.5	20228.1	4	5	14	+0.5
21068.6	5	17	6	−0.9	20707.4	6	3	4	+0.1	20209.0	4	6	15	+0.4
21062.1	10	10	2	−0.6	20701.3	5	6	6	+0.1	20192.8	4	4	14	+0.5
21059.3	5	15	5	−1.3	20691.3	6	1	3	−0.4	20190.7	4	7	16	+0.9
21051.2	9	8	1	+0.2	20686.4	5	4	5	−0.4	20182.4				
21039.3	7	6	0	+0.9	20680.4	4	7	7	−0.1	20173.9	4	5	15	+0.2
21038.8	6	11	3	−1.3	20671.6	6	2	4	0.0	20172.3	3	8	17	+1.5
21036.2	4	16	6	−1.0	20666.2	5	5	6	−0.1	20155.4	4	6	16	+0.4
21028.7	8	9	2	0.0	20654.8	7	0	3	−0.7	20138.8	3	4	15	+0.4
21017.1	7	7	1	+0.5	20651.3	6	3	5	−0.1	20137.3	4	7	17	+0.9
21005.4	6	10	3	−1.0	20645.6	5	6	7	−0.1	20120.2	4	5	16	+0.1
21004.2	6	5	0	+0.7	20639.4	5	9	9	−0.6	20119.2	3	8	18	+1.5
20994.6	7	8	2	+0.1	20635.2	6	1	4	−0.4	20113.3	3	11	20	−0.7
20982.1	8	6	1	+0.3	20631.4	5	4	6	+0.4	20109.8				
20972.1	6	9	3	−0.3	20625.1	4	7	8	0.0	20102.0	4	6	17	+0.4
20968.8	8	4	0	+0.6	20616.3	6	2	5	+0.6	20085.0	3	4	16	+0.2
20960.1	6	7	2	0.0	20610.9	5	5	7	+0.1	20084.2	4	7	18	+0.9
20955.4	6				20598.8	7	0	4	−0.6	20066.3	4	8	19	+1.5
20949.6	6	10	4	−0.7	20596.3	5	3	6	+0.7	20049.0	4	6	18	+0.5
20947.1	7	5	1	+0.2	20590.1	4	6	8	−0.2	20031.3	4	7	19	+0.9
20942.1	5				20584.5	4	9	10	+0.9	20026.2	4	10	21	−1.7
20938.5	5	8	3	+0.3	20579.8	6	1	5	+0.1	20013.8	4	8	20	+1.7
20933.2	8	3	0	+0.4	20576.1	5	4	7	+0.6	20009.6				
20925.2	6	6	2	−0.1	20560.4	6	2	6	+0.5	19996.2	4	6	19	+0.6
20920.7	5				20555.7	5	5	8	+0.3	19978.7	4	7	20	+0.8
20916.2	6	9	4	−0.1	20543.1	6	0	5	−0.4	19961.4	4	8	21	+1.8
20911.9	5	4	1	+0.3	20541.1	6	3	7	+1.0	19943.8	4	6	20	+0.9
20903.7	5	7	3	−0.1	20523.8	4	1	6	−0.1	19926.7	4	7	21	+1.5
20897.3	7	2	0	+0.2	20521.1	5	4	8	+1.0					

C. The products and energies of dissociation

It is well known that the energy of dissociation of molecules may be obtained by means of extrapolation. The vibrational intervals ΔT are plotted against the upper vibrational terms for the violet system in Fig. 3, and against the upper and lower vibrational terms for the blue system in Figs. 4 and 5, respectively. The circles represent the experimental points, the full curves correspond to the intervals as well as terms calculated from Eqs. (1) and (2). As usually in cases of alkali molecules NaK, Cs_2[9, 11] etc., the

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[11] Loomis and Arvin, Phys. Rev. **46**, 286 (1934).

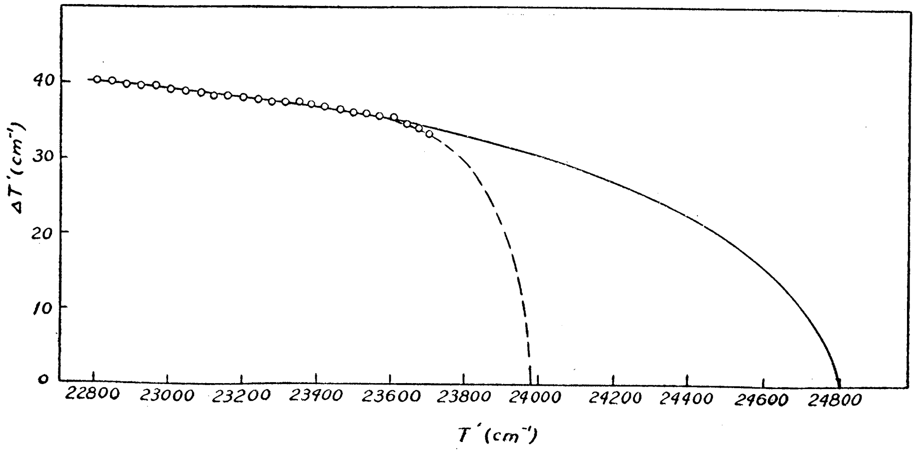

FIG. 3. $\Delta T'$ *vs.* T' for the violet system.

last experimental points begin to drop below the curves so that the values of T at which the curves strike the axes can be taken as the maximum values of the energies of dissociation. That is, $T_v' < 24800$ cm^{-1} for the violet system, $T_b' < 23520$ cm^{-1} for the blue system and $T'' < 4250$ cm^{-1}. On the other hand, since the experimental values of T are far from converging, it seems probable that the minimum values of the energies of dissociation are given by the dashed curves, which yield $T_v' > 23980$ cm^{-1}, $T_b' > 22270$ cm^{-1} and $T'' > 3500$ cm^{-1}.

Let us first take temporarily the mean value of $T'' = 3880$ cm^{-1} as the energy of dissociation of the lower state, D_e'', and see what will be the products of dissociation of the two upper states. The difference of T' and T'' is the atomic energy T_a, so we have 20920 cm$^{-1} > T_a > 20100$ cm^{-1} for the violet system and 19640 cm$^{-1} > T_a > 18390$ cm^{-1} for the blue system. The products of dissociation of the ground state of the molecule are two normal ($5s$, ^2S) rubidium atoms. From the limiting values of atomic energies, we may conclude that the upper state of the violet system dissociates into one atom in the normal state ($5s$, ^2S) and one atom in the excited state ($6s$, ^2S), while that of the blue system into one in the normal state and one in the excited state ($4d$, ^2D), though such transitions are forbidden in the atomic spectra.

Now we come to determine accurately the value of energy of dissociation of the ground state by using the known values of the atomic energies and the experimental data. From the lower state, we have 3500 cm$^{-1} < D_e'' < 4250$ cm^{-1}, and from the upper states of the violet and blue systems we get 3850 cm$^{-1} < D_e'' < 4670$ cm^{-1} and 2920 cm$^{-1} < D_e'' < 4170$ cm^{-1}, respectively. According to the three pairs of the limiting values of D_e'', we may conclude that

$$3850 \text{ cm}^{-1} < D_e'' < 4170 \text{ cm}^{-1}.$$

The actual energy of dissociation D_0 is thus given by

$$3820 \text{ cm}^{-1} < D_0'' < 4140 \text{ cm}^{-1},$$

or in the unit of electron volt,

$$0.47 \text{ volt} < D_0'' < 0.51 \text{ volt}.$$

We take the mean value $D_0'' = 0.49$ volt and feel confident that it is not in error by more than 0.02 volt.

From this value for the ground state, the

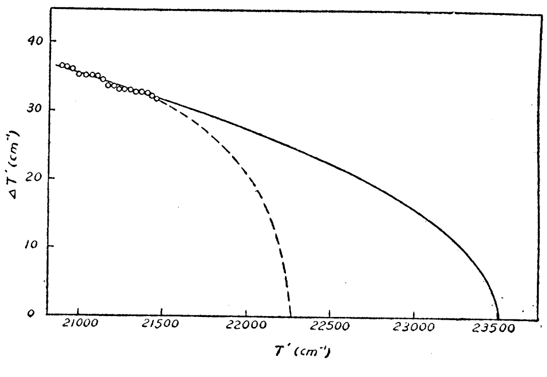

FIG. 4. $\Delta T'$ *vs.* T' for the blue system.

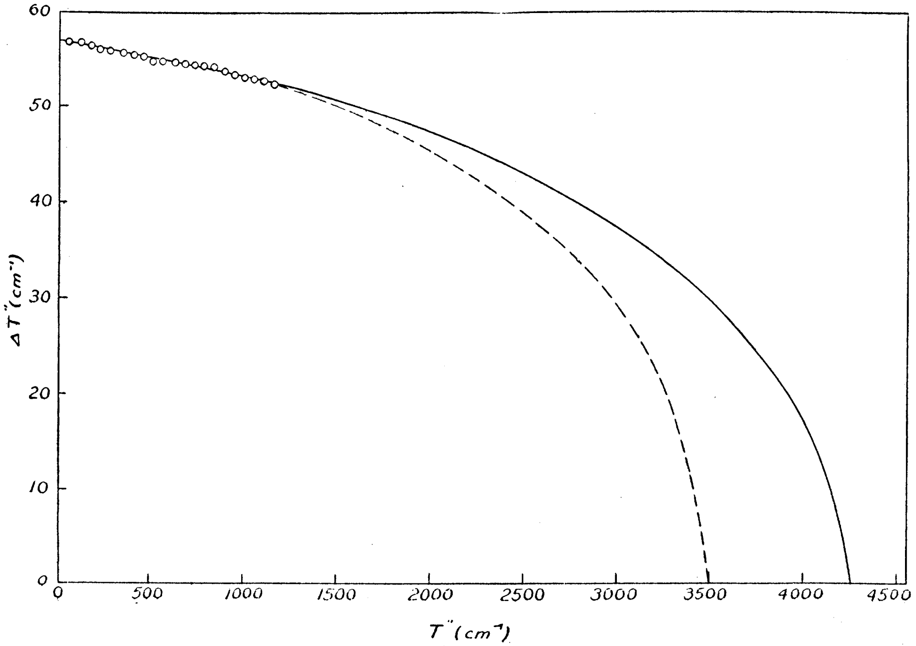

FIG. 5. $\Delta T''$ *vs.* T'' for the blue system.

energy of dissociation of the upper state of the violet system is calculated to be 0.17 volt and that of the blue system to be 0.31 volt.

DISCUSSION

The value of energy of dissociation of the ground state of Rb_2 thus determined agrees, within experimental errors, with that obtained by interpolation from the energies of other alkali molecules (0.47 volt). Although the products and energies of dissociation of the upper states of the two systems are determined in this investigation, we still cannot draw any conclusion about the molecular states of the two levels.

The blue and violet systems of Rb_2 are similar to the blue band system of K_2 reported by Yamamoto[12] and the blue-green system of Cs_2 reported by Loomis and Kusch,[9] of which neither the energy of dissociation nor the molecular state was definitely determined. Owing to the similarity between the edge at 5223A of Cs_2 and the edges of $^1\Sigma \leftarrow {}^1\Sigma$ systems of Li_2, Na_2 and K_2, Loomis and Kusch thought that the blue-green system of Cs_2 was very likely a $^1\Sigma \leftarrow {}^1\Sigma$ system associated with the second doublet of the principal series of caesium. But this argument cannot hold, at least in the present case, because the necessary conditions for the existence of an edge explained by Loomis and Nile[13] namely, $\omega_e'' > \omega_e'$ and $D'' < D'$ are only half fulfilled. So the question about the molecular states of the systems is still open. We write arbitrarily $D \leftarrow {}^1\Sigma$ for the blue system and $E \leftarrow {}^1\Sigma$ for the violet system.

Finally let us compare our results with the work of Matuyama.[6] All band heads in his data coincide approximately with our strong heads, but none of the weaker bands in our data, especially those with high quantum numbers, has been observed by him. The analysis made by him appears to be erroneous partly due to the incompleteness of his data and partly due to the mistake in the arrangement of the square array.

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[12] Yamamoto, Nat. Research Council Japan **5**, 146 (1929).

[13] Loomis and Nile, Phys. Rev. **32**, 873 (1932).