

MAGNETIC ROTATION SPECTRUM AND HEAT OF DISSOCIATION OF THE POTASSIUM MOLECULE

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ABSTRACT

The magnetic rotation spectrum of the near red, ${}^4\Pi\leftarrow{}^1\Sigma$ band system of K_2 has been photographed with the apparatus previously used for Li_2 . In this way the series of upper vibrational levels has been extended from the 16th, the last one observed by Crane and Christy, to the 27th. This permits an accurate extrapolation to convergence, which is estimated to occur at $v'=31.6$, the corresponding energy being $17160\text{ cm}^{-1}=2.12$ volts. It follows that the heat of dissociation of the normal molecule is 0.51 ± 0.02 volt. From this and other data the percentage of molecules in the vapor at various temperatures is calculated. An improved Franck-Condon diagram for the red and infrared systems of K_2 has been constructed. It gives a good representation of the observed distribution of bands and predicts the existence of an infrared edge. This is confirmed by observation. Magnetic rotation spectra have been found in the regions of the infrared and blue ${}^1\Sigma\leftarrow{}^1\Sigma$ systems. They are probably analogous to the red magnetic rotation spectrum of sodium, and like it, are not yet understood.

THE apparatus which we constructed¹ and used to study the magnetic rotation spectrum of Li_2 has now been used on that of K_2 with the same object, that is, to measure the vibrational levels which come nearest to dissociation and to extrapolate them to find the energy of dissociation of the molecule. The apparatus, with a long column of vapor inside a solenoid, was designed to bring out the weak lines corresponding to these levels, and was successful in doing so in the case of lithium.

The spectrum obtained in the region of the red (${}^4\Pi\leftarrow{}^1\Sigma$) system of potassium is shown in Fig. 1. In this figure the values of the quantum number v'' which have been assigned to the bands are indicated above them and the changes of quantum number, $v'-v''$, for the various sequences are indicated below. The spectrum was photographed with sunlight as a source. The comparison spectrum is neon. The continuum on the short-wave side is due to the magnetic rotation of the D lines of sodium which was present as an impurity. In the region where this comes near to the short wave end of the potassium rotation spectrum the absorption bands of potassium can be seen against it. The very strong line between the -5 and -6 sequences is the resonance doublet of atomic lithium which was also present as an impurity. The resonance doublet of potassium is far off the plate to the right. It will be seen that, as was the case with lithium, our method of observation brings out not only the heads of the bands but also a little structure on the long wave-length side of the stronger bands.

¹ Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931).

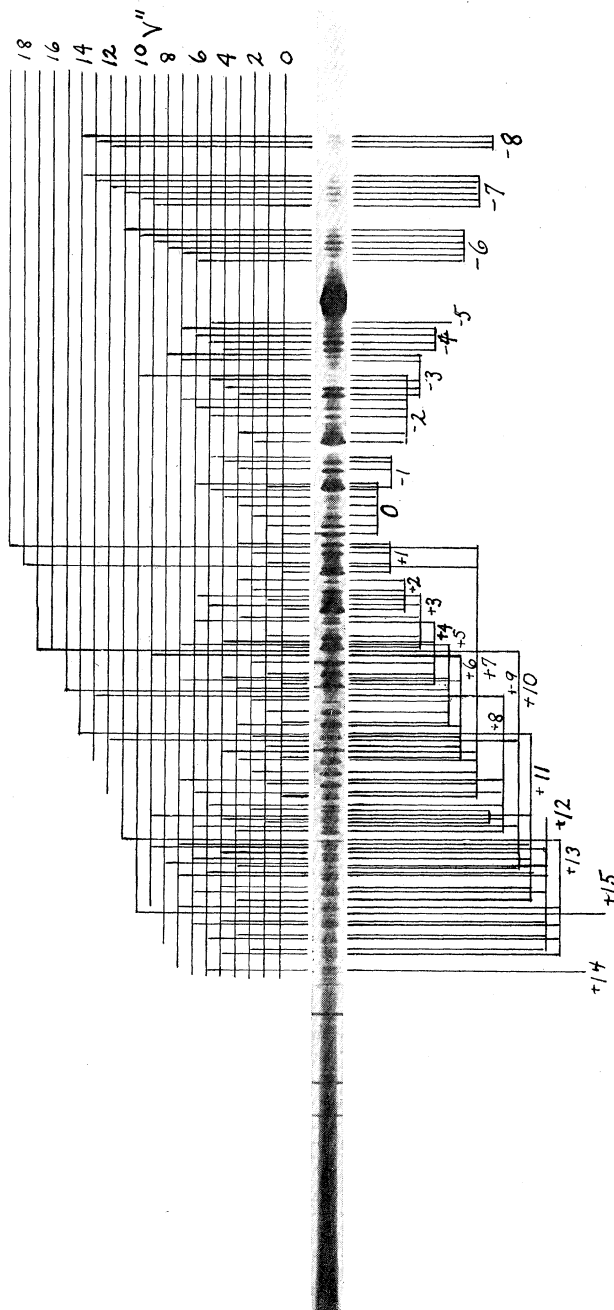


Fig. 1. The magnetic-rotation spectrum of K_2 .

Table I gives the frequencies of all measured band heads with the exception of a very few weak ones and perhaps one or two that could not be distinguished from structural lines of strong bands. In many cases the frequen-

TABLE I

v'	v''	In- tensity	Ob- served	Calcu- lated	Observed- Calcu- lated	v'	v''	In- tensity	Observed	Calcu- lated	Observed- Calcu- lated
22	6	0	16285.86	16283.61	+2.25	26	15	0	15717.63	15731.37	-13.74
18	4	0	16227.84	16228.58	-0.74	6	1	4	15711.86	15711.77	+0.09
21	6	0	16227.84	16227.28	+0.56	7	2	4	15690.78	15690.50	+0.28
24	8	0	16217.69	16217.61	+0.08	25	15	1	15674.44	15680.75	-6.31
19	5	2	16198.34	16199.35	-1.01	8	3	2	15669.19	15669.21	-0.02
17	4	2	16168.31	16167.68	+0.63	4	0	7	15660.70	15661.72	-1.02
14	2	2	16159.97	16159.46	+0.51	13	7	0	15650.80	15649.30	+0.50
18	5	3	16139.80	16139.48	+0.32	9	4	1	15647.23	15647.91	-0.68
21	7	3	16139.80	16139.60	+0.20	5	1	5	15641.04	15641.13	-0.09
15	3	1	16131.91	16132.71	-0.80	6	2	3	15619.57	15620.55	-0.98
24	9	1	16131.91	16131.33	+0.58	15	9	1	15603.82	15604.45	-0.63
19	6	4	16111.70	16110.95	+0.75	27	17	1	15597.04	15618.43	-21.39
16	4	3	16105.48	16105.76	-0.28	3	0	10	15589.28	15589.68	-0.40
25	10	1	16091.96	16097.95	-5.99	12	7	3	15582.92	15583.83	-0.91
20	7	2	16082.46	16082.02	+0.44	8	4	3	15578.94	15579.39	-0.45
14	3	2	16069.39	16068.94	+0.45	4	1	4	15569.09	15569.78	-0.69
18	6	4	16051.15	16051.08	+0.07	10	6	4	15538.84	15538.20	+0.64
15	4	2	16042.88	16042.89	-0.01	6	3	2	15529.68	15530.03	-0.35
19	7	4	16023.48	16023.27	+0.21	2	0	15	15516.43	15516.90	-0.47
22	9	4	16023.48	16022.67	+1.81						
16	5	4	16016.56	16016.66	-0.10	7	4	5	15511.01	15510.16	+0.85
13	3	2	16003.24	16004.30	-1.06	3	1	4	15496.71	15497.74	-1.03
20	8	0	15996.50	15995.04	+1.46	12	8	4	15496.71	15496.85	-0.14
17	6	2	15990.10	15990.18	-0.08	8	5	2	15490.32	15490.29	+0.03
14	4	3	15978.54	15979.12	-0.58	4	2	7	15478.29	15478.56	-0.27
21	9	2	15968.35	15966.34	+2.01	5	3	3	15459.80	15459.39	+0.41
18	7	2	15962.21	15963.40	-1.19	1	0	10	15443.15	15443.41	-0.26
						25	18	4	15433.34	15438.93	-5.59
24	11	2	15960.08	15960.91	-0.83	2	1	2	15426.18	15424.96	+1.22
12	3	7	15937.81	15938.83	-1.02	3	2	8	15405.26	15406.52	-1.26
22	10	7	15937.81	15937.11	+0.70	26	19	1	15397.29	15409.95	-12.66
19	8	7	15937.81	15936.29	+1.52	4	3	8	15388.44	15388.04	+0.40
16	6	3	15928.30	15928.26	+0.04	0	0	7	15369.04	15369.18	-0.14
25	12	1	15923.61	15928.95	-5.34	5	4	7	15369.04	15369.57	-0.53
27	13	1	15923.61	15945.11	-21.50	1	1	10	15351.59	15351.47	+0.12
13	4	3	15914.61	15914.48	+0.13	6	5	10	15351.59	15351.11	+0.48
20	9	1	15908.83	15908.76	+0.07	2	2	3	15333.18	15333.74	-0.56
23	11	1	15908.83	15907.28	+1.55	3	3	2	15315.38	15316.00	-0.62
10	2	6	15896.26	15896.04	+0.22	4	4	1	15297.82	15298.22	-0.40
14	5	4	15888.47	15890.02	-1.55	5	5	1	15281.37	15280.47	+0.90
7	0	5	15873.22	15873.66	-0.44	0	1	15	15276.96	15277.24	-0.28
11	3	5	15873.22	15872.56	+0.66	6	6	2	15261.82	15262.71	-0.89
15	6	3	15865.99	15865.39	+0.60	2	3	10	15243.54	15243.22	+0.32
8	1	11	15849.43	15850.95	-1.52	3	4	4	15226.28	15226.18	+0.10
12	4	11	15849.43	15849.01	+0.42	4	5	0	15209.65	15209.12	+0.53
19	9	11	15849.43	15850.01	-0.58	0	2	20	15186.02	15186.02	0.00
16	7	0	15841.91	15840.58	+1.33	1	3	5	15170.54	15169.73	+0.81
9	2	12	15827.27	15828.25	-0.98	3	5	3	15136.67	15137.08	-0.41
13	5	12	15827.27	15825.38	+1.89	4	6	4	15119.99	15120.72	-0.73
6	0	10	15804.41	15803.71	+0.70	5	7	0	15105.14	15104.39	+0.75
10	3	10	15804.41	15805.52	-1.11						
						10	11	0	15105.14	15106.84	-1.70
26	14	1	15799.49	15813.39	-13.90	0	3	10	15095.90	15095.50	+0.40
14	6	1	15799.49	15801.62	-2.13	1	4	10	15080.12	15079.91	+0.21
24	13	1	15793.61	15793.33	+0.28	2	5	1	15064.63	15064.30	+0.33
22	12	2	15768.63	15768.11	+0.52	8	10	0	15055.06	15055.39	-0.33
8	2	4	15760.06	15759.73	+0.33	4	7	0	15032.28	15033.04	-0.76
25	14	3	15755.80	15762.77	-6.97	5	8	2	15017.09	15017.41	-0.32
9	3	4	15737.03	15737.73	-0.70	0	4	6	15004.91	15005.68	-0.77
13	6	4	15737.03	15736.98	+0.05	1	5	8	14989.90	14990.81	-0.91
5	0	4	15732.46	15733.07	-0.61	2	6	5	14975.82	14975.90	-0.08
10	4	0	15717.63	15715.70	+1.93	3	7	4	14962.04	14961.00	+1.04

TABLE I (Continued)

v'	v''	In- tensity	Observed	Calcu- lated	Observed- Calcu- lated	v'	v''	In- tensity	Observed	Calcu- lated	Observed- Calcu- lated
3	8	2	14873.67	14874.02	-0.35	3	10	2	14702.57	14702.18	+0.39
4	9	1	14858.41	14859.78	-1.37	4	11	2	14689.71	14689.36	+0.35
0	6	0	14827.49	14828.18	-0.69	5	12	2	14676.74	14676.57	+0.17
1	7	2	14813.87	14814.73	-0.86	6	13	1	14663.24	14663.77	-0.53
2	8	4	14801.63	14801.24	+0.39	7	14	1	14651.23	14650.98	+0.25
3	9	5	14788.86	14787.74	+1.12	3	11	0	14617.43	14617.30	+0.13
4	10	3	14774.80	14774.22	+0.58	4	12	0	14604.86	14605.22	-0.36
5	11	2	14761.70	14759.77	+1.93	6	14	0	14581.46	14581.03	+0.43
6	12	1	14746.63	14747.21	-0.58	7	15	0	14567.87	14568.96	-1.09
2	9	1	14715.62	14714.96	+0.66						

cies are approximately the same as those of absorption bands reported by Crane and Christy,² but our measurements extend considerably further toward the short wave-lengths and also much further toward high quantum numbers. The highest value of v' reported by Crane and Christy is 16, whereas we have identified bands up to $v' = 27$, which according to our estimate below, comes within 5 levels of convergence. The quantum numbers which we have assigned to the bands measured by Crane and Christy are the same as theirs in all but one or two cases. The extension of the assignment to the higher numbered bands was carried out by a process of extrapolation by differences and was checked by the combination relation.

We were not able to identify any bands due to the isotopic molecule $K^{39}K^{41}$. This was doubtless due to the comparative scarcity of such molecules and to the smallness of the isotopic displacement.

The extension of the spectrum to higher values of v' made necessary a revision of Crane and Christy's formula. It was found that their formula for the v'' terms is adequate, but that for the v' terms had to be changed. It was found impossible to represent all the upper level terms by a polynomial of reasonably low degree. Eq. (1)

$$\begin{aligned} \nu = & 15378.01 + 75.00(v' + \frac{1}{2}) - 0.3876(v' + \frac{1}{2})^2 \\ & + 0.004366(v' + \frac{1}{2})^3 - 0.0001830(v' + \frac{1}{2})^4 - 92.64(v'' + \frac{1}{2}) \\ & + 0.354(v'' + \frac{1}{2})^2 \end{aligned} \quad (1)$$

however, was found to be satisfactory for all bands with v' less than 25, and the values in the fifth column of Table I are calculated on the basis of Eq. (1), as are also the residuals in the sixth column. It will be seen, however, from column 6 and also from Fig. 2, in which the residuals from Eq. (1) are plotted against v' , that Eq. (1) is completely inadequate to represent the terms with $v' \geq 25$. Eq. (2)

$$\begin{aligned} \nu = & 15379.44 + 72.870(v' + \frac{1}{2}) + 0.2535(v' + \frac{1}{2})^2 \\ & - 0.06916(v' + \frac{1}{2})^3 + 0.0033472(v' + \frac{1}{2})^4 - 0.00005986(v' + \frac{1}{2})^5 \\ & - 92.64(v'' + \frac{1}{2}) + 0.354(v'' + \frac{1}{2})^2 \end{aligned} \quad (2)$$

² Crane and Christy, Phys. Rev. **36**, 421 (1930).

is a least squares representation of the whole series of measured v' levels. It is represented by the curve in Fig. 2. It will be seen that it represents the levels 25–27 adequately and, indeed, represents all levels fairly well, but that it is inferior to Eq. (1) as a representation of the levels 0–24. Eq. (1) may, therefore, be considered as the best available representation of the constants of the molecule near the equilibrium point, whereas the extrapolation to dissociation can best be based on Eq. (2).

The extrapolation of the upper levels to convergence is shown in Fig. 3, wherein $\Delta\nu$, the difference between successive vibrational levels of the upper state, is plotted against T' the energy corresponding to the average of the two levels. The curve represents Eq. (2) which, as has just been pointed out,

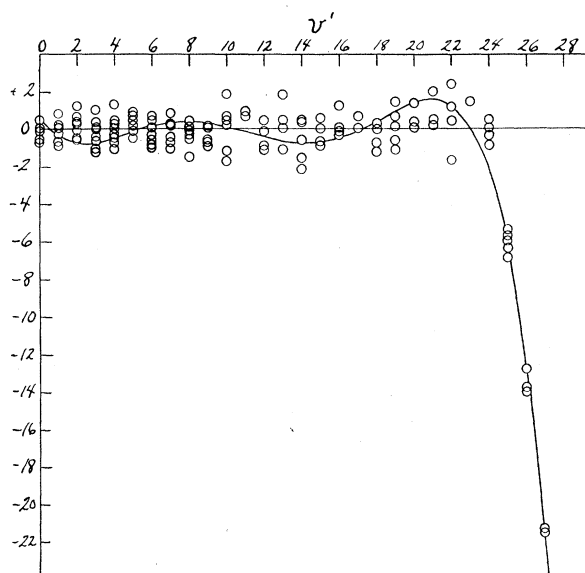


Fig. 2. Residuals of observed frequencies from Eq. (1). The curve represents Eq. (2).

is superior to Eq. (1) for high quantum numbers and for the extrapolation and which, for lower quantum numbers does not differ from Eq. (1) by enough to show on the scale of Fig. 3. It will be noted that the highest observed level lies within 0.02 volt of the estimated convergence and also that it would be difficult to make a reasonable extrapolation which would lie more than 0.02 volt above the estimated convergence, so that it may be said that the value of the energy of dissociation estimated by extrapolation according to Eq. (2) may be relied upon to within 0.02 volt.

According to Eq. (2) convergence occurs at $v' = 31.6$ and the corresponding maximum of T' , that is the energy of the atoms into which the upper level dissociates, is 17160 cm^{-1} .

The energies of an excited potassium atom in the lowest 2P states are 12985 and 13043 cm^{-1} . Since it is uncertain into which of these the excited

molecule dissociates and since the difference between them is somewhat less than the probable error of the extrapolation, it is sufficient to take the energy of the excited atom as the average, namely, 13014 cm^{-1} . The resulting value for the energy of dissociation of the normal molecule is $4146 \text{ cm}^{-1} = 0.51 \text{ volt}$.

The value for the heat of dissociation calculated by Crane and Christy from their much shorter series of levels was 0.81 volt. It seems to be a general fact that too long an extrapolation is likely to lead to too high a value of the energy of dissociation.

Several other estimates of the energy of dissociation of the normal K_2 molecule have been published. Carelli and Pringsheim,³ as the results of two

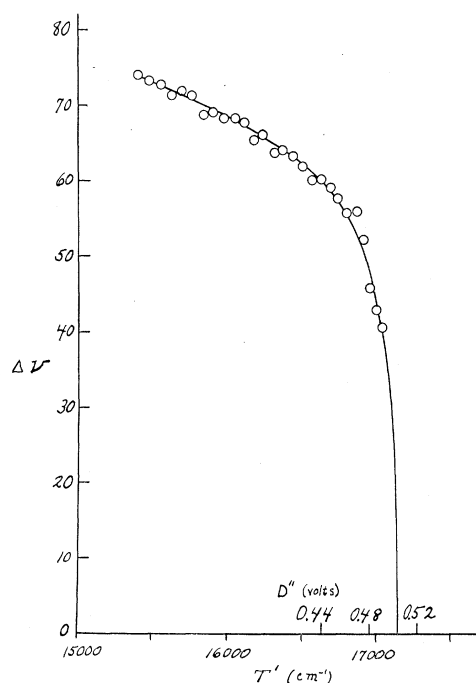


Fig. 3. Δv vs. T' plotted and extrapolated to dissociation following Eq. (2). Upper scale of abscissae represents values of D_0'' which would be deduced from corresponding T' intercepts.

somewhat different experiments, find the values 0.63 volt and 0.53 volt. However, Crane and Christy² have made a critical study of Carelli and Pringsheim's experiments and conclude that they may be in error by as much as 0.3 volt. Dichtburn⁴ and Walter and Barratt⁵ make the assumption that certain diffuse bands in the spectra of Na_2 , K_2 , Rb_2 , Cs_2 , etc., are similar to the iodine continuum at 5000A and are to be interpreted as due to transitions from the lower state to the dissociated upper state. They deduce the values

³ Carelli and Pringsheim, *Zeits. f. Physik* **55**, 643 (1927).

⁴ Dichtburn, *Proc. Roy. Soc.* **A117**, 486 (1928).

⁵ Walter and Barratt, *Proc. Roy. Soc.* **A119**, 257 (1928).

0.14, 0.53, 1.02 and 0.91 or 1.17 volts for the heats of dissociation of Na_2 , K_2 , Rb_2 and Cs_2 , respectively. However, these values for the Na_2 , Rb_2 and Cs_2 molecules are absurdly far from the true ones. Moreover, they tacitly assume that the transitions accompanying the continua start from the 0 vibrational level of the lower states as they do in iodine, whereas Fig. 5 shows that they must start from a lower vibrational state having, in the case of K_2 , some 0.3 volt vibrational energy. It may reasonably be concluded that their agreement

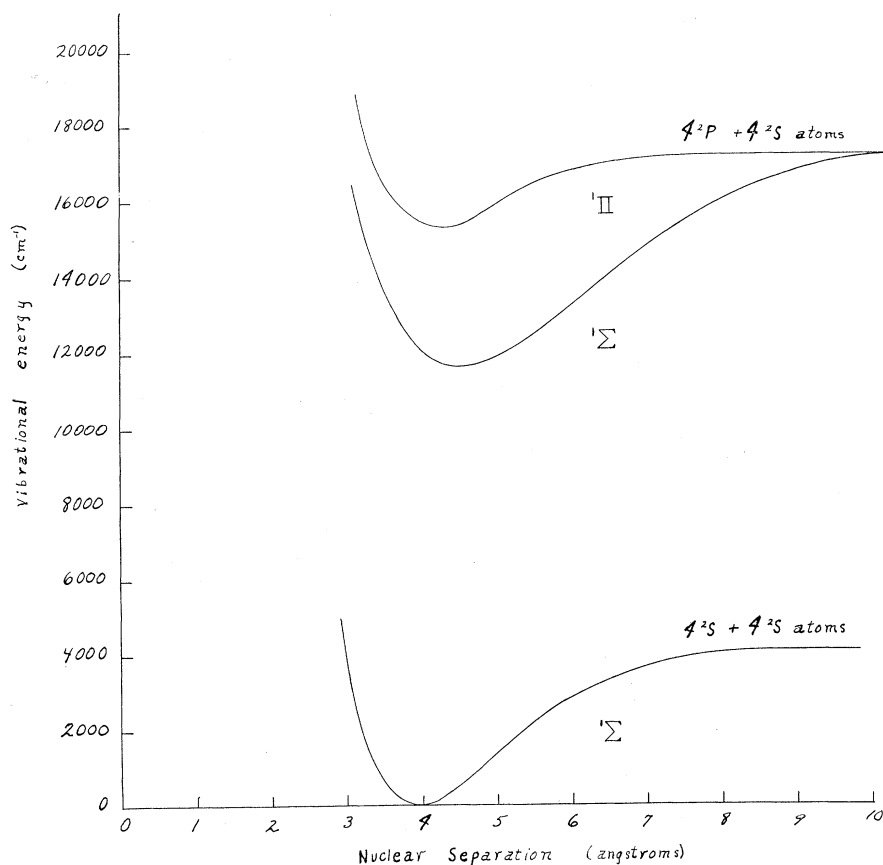


Fig. 4. Potential energy curves for the lowest three known levels of K_2 .

with our value in the case of K_2 is wholly fortuitous. The significance of the observed continua remains obscure.

Probably the best chemical determination of the heat of dissociation of potassium is that of Lewis⁶ who measured the ratio of molecules to atoms in a molecular beam and found that the value of the heat of dissociation which, when put into Gibson and Heitler's formula,⁷ gave the best representation of his data, was 0.62 ± 0.04 volt. Unfortunately he took for the moment of

⁶ Lewis, *Zeits. f. Physik* **69**, 786 (1931).

⁷ Gibson and Heitler, *Zeits. f. Physik* **49**, 465 (1928).

inertia the value $184 \times 10^{-40} \text{ g} \cdot \text{cm}^2$ which is from the old discredited⁸ work of Smith.⁹ The true value¹⁰ is $492 \times 10^{-40} \text{ g} \cdot \text{cm}^2$. We have recalculated his data, with the correct value of the moment of inertia, and find for the energy of dissociation 0.56 volt which differs from ours by very little more than the 0.04 volt which he claims as his probable error.

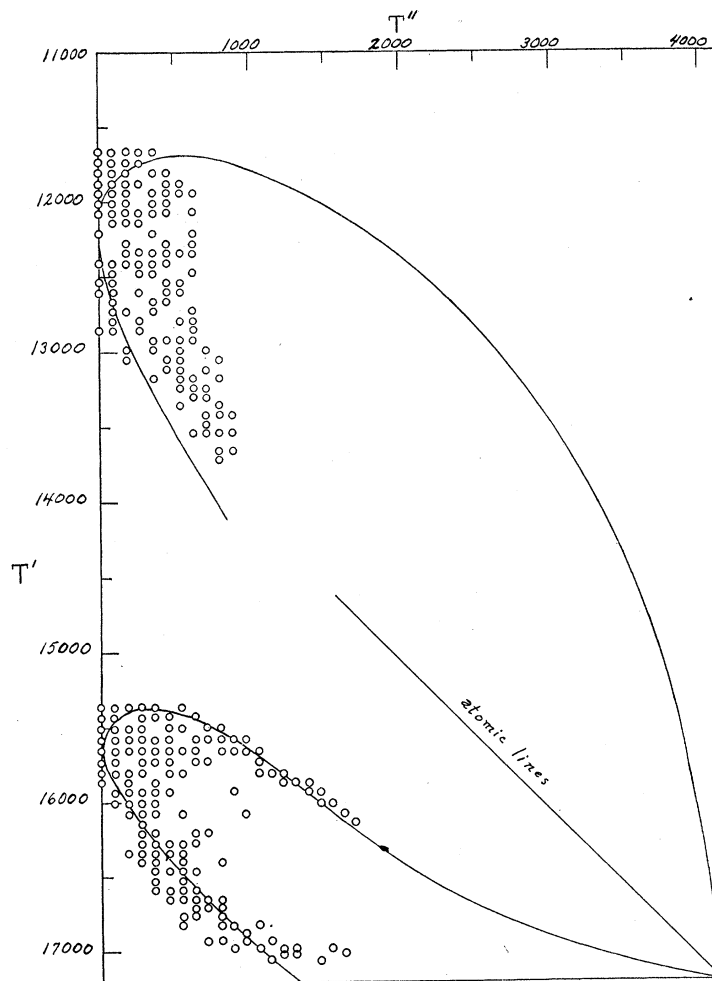


Fig. 5. Improved Franck-Condon diagram for the red and infrared systems. Lines of constant frequency have 45° slope.

The heat of dissociation has also been estimated by Ootuka¹¹, on the basis of experiments with low pressure flames, as 0.53 volt, which is an average of a selection of a number of values ranging from 0.51 to 0.66 volt.

⁸ Loomis and Wood, *Phys. Rev.* **32**, 223 (1928).

⁹ Smith, *Proc. Roy. Soc.* **A106**, 400 (1924).

¹⁰ Loomis, *Phys. Rev.*, in press.

¹¹ Ootuka, *Zeits. f. phys. Chem.* **B7**, 422 (1930).

Fig. 4 shows the potential energy curves of the three lowest states of K_2 as based on our value, 0.51 volt, for the energy of dissociation and on the constants of the molecule deduced by Loomis¹⁰ in his rotational analysis of the spectrum.

Fig. 5 is a Franck-Condon diagram, in the improved form described in our paper on lithium,¹ for the red and infrared band systems of potassium. The circles in the case of the red system represent the magnetic rotation bands as observed by us. In the case of the infrared system they represent the absorption bands reported by Crane and Christy. The curves deduced from Fig. 4 give a good representation of the intensity distribution, which is a confirmation of the correctness of the rotational analysis and of our value of the energy of dissociation.

It will be noted that there should be a sharp edge to the infrared band system at about $10,300\text{ cm}^{-1} = 9700\text{A}$. To check this point the absorption spectrum was photographed in this region. A rather sharp edge was found at $10600\text{A} = 9450\text{ cm}^{-1}$. The difference between this and the calculated location is probably partly due to inaccuracy of the parts of the potential energy curves which are connected with the edge and partly to the fact that the edge may be beyond the maximum of intensity.

In column 3 of Table II are the values of the mass action coefficient, in millimeters of mercury, for the dissociation, calculated according to the equation of Gibson and Heitler,⁷ with the data in this paper and Loomis' value, $492 \times$

TABLE II.

$T^\circ\text{C}$	P in mm of Hg	K	α	$T^\circ\text{C}$	P in mm of Hg	K	α
100°C	0.0000183	0.3013	0.999878	500	28.07	1709.	0.9687
150	0.000490	2.138	0.99954	600	127.4	4374.	0.9464
200	0.00655	10.08	0.9987	700	423.6	9325.	0.9199
300	0.290	115.1	0.9950	757.3	760.0	13439.	0.9031
400	3.95	506.9	0.9848				

10^{-40} , for the moment of inertia of the normal K_2 molecule. The corresponding vapor pressures of potassium, taken from the data as reported by Fiock and Rodebush¹² and by Edmondson and Edgerton,¹³ are given in column 2. In column 4 are given the corresponding values of α , the degree of dissociation of the molecules into atoms. The relation between K and α is

$$K = \frac{4\alpha^2}{1 - \alpha^2} p. \quad (3)$$

An attempt was made to settle the question as to whether the $^1\Sigma - ^1\Sigma$ band system actually gives a magnetic rotation spectrum, as it appears to do in the case of sodium, although present theories indicate that it should not. By a long exposure with a rather wide slit, with a neocyanine plate, we suc-

¹² Fiock and Rodebush, Jour. Am. Chem. Soc. **48**, 2522 (1926).

¹³ Edmondson and Edgerton, Proc. Roy. Soc. **A113**, 520 (1927).

ceeded in photographing what appears to be a magnetic rotation spectrum in the neighborhood of the infrared ($^1\Sigma - ^1\Sigma$) system of K_2 . As in the case of sodium, it has no simple relation to the absorption spectrum; at least, the magnetic rotation lines do not coincide with the absorption heads as they do in the $^4\Pi - ^1\Sigma$ system. Another magnetic rotation spectrum, which likewise has no simple relation to the absorption spectrum, was found in the region of the blue system which lies on the long-wave side of the second line of the principal series and is probably also a $^1\Sigma - ^1\Sigma$ transition.

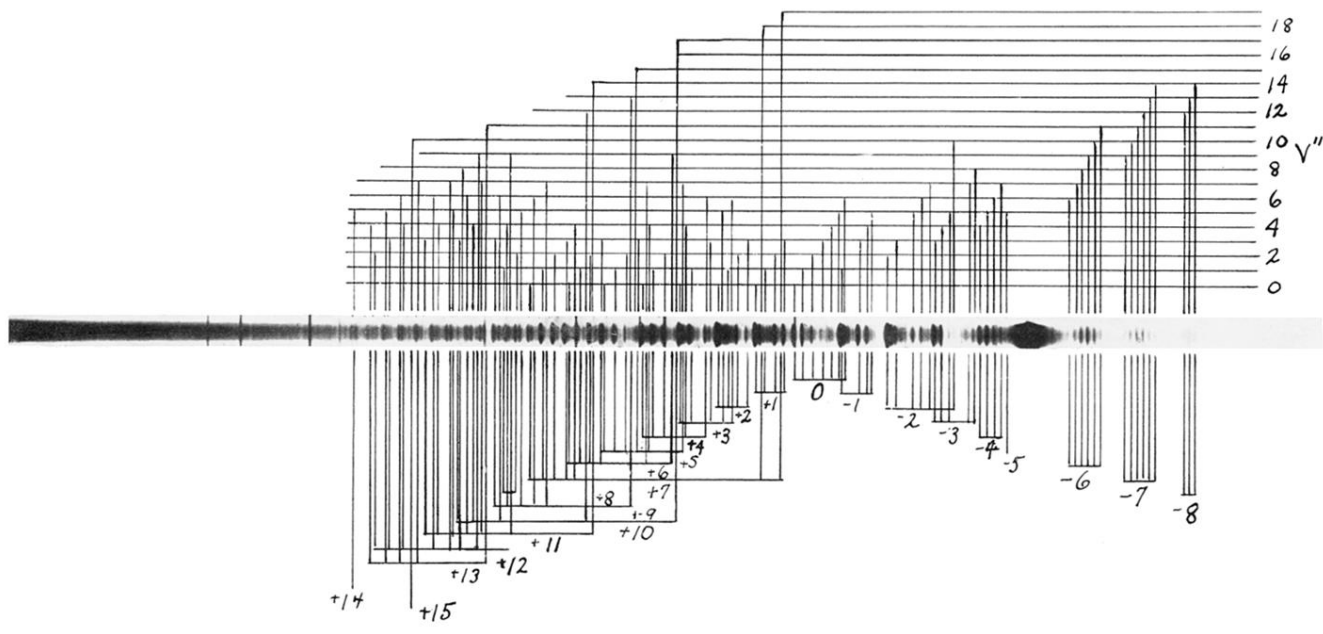


Fig. 1. The magnetic-rotation spectrum of K_2 .