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VIBRATIONAL QUANTUM ANALYSIS OF THE POTASSIUM INFRARED ABSORPTION BANDS

By W. O. Crane and Andrew Christy

Ryerson Physical Laboratory, University of Chicago

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Abstract

The heads of the red system of the K_2 molecule have been remeasured, and twenty six new bands have been found. The vibrational constants derived from our measurements are: $\omega_e''=92.64$ cm^{-1}, $\omega_e''x''=0.354$ cm^{-1}, $\omega_e'=74.73$ cm^{-1}, and $\omega_e'x'=0.327$ cm^{-1}.

The bands of the infrared system of K_2 (λ7735 to λ8850) have been measured and a new vibrational analysis for this system is given, which removes the objections inherent in the analysis of Ritschl and Villars. The constants for this system, as found by us, are: $\omega_e''=92.64$ cm^{-1}, $\omega_e''x''=0.354$ cm^{-1}, $\omega_e'=69.09$ cm^{-1}, and $\omega_e'x'=0.153$ cm^{-1}. It is shown that the upper state of each of the two systems dissociates into a normal and a ^2P excited atom. The energies of dissociation obtained for the upper levels of the two systems agree to within 0.02 volts, the average value being 2.41 volts. From this average value we obtain for the heat of dissociation of the lower level 0.81 volts, while from the formula $(\omega_e'')^2/4\omega_e''x''$, we obtain 0.75 volts.

THE absorption spectrum of the K_2 molecule thus far investigated contains three band systems: in the blue, $D\leftarrow A^1\Sigma$, (λ4243 to λ4613), in the red, $C^1\Pi\leftarrow A^1\Sigma$ (λ6280 to λ6925), and in the infrared, $B^1\Sigma\leftarrow A^1\Sigma$(λ7735 to λ8850).

The vibrational analysis of the blue system has been given by Yamamoto[1,2] The equation of the band heads in terms of half quantum numbers is:

$$\nu = 22970.0 + 61.28(v' + \tfrac{1}{2}) - 0.24(v' + \tfrac{1}{2})^2 - 92.54(v'' + \tfrac{1}{2}) + 0.353(v'' + \tfrac{1}{2})^2 \quad (1)$$

The red system, $C^1\Pi\leftarrow A^1\Sigma$, was analyzed by Fredrickson and Watson.[3] The equation connecting the heads in terms of half quantum numbers is:

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

The equation actually given is:

$$\nu=22954.6+(61.13n'-0.24n'^2)-(91.96n''-0.32n''^2)$$

The constants for the equation, according to Yamamoto, were obtained by the least square method. However, there must have been some error in the calculation of ω_0'' and $\omega_0''x''$. When the least square method is applied to all the intervals as actually obtained from the heads given in the paper the authors find: $\omega_0''=92.19$ cm^{-1} and $\omega_0''x''=0.353$ cm^{-1}. These values are used in Eq. (1). These corrected values of the constants ω_0'' and $\omega_0''x''$ agree exactly with the constants as derived by the authors from the two other systems.

[2] See also W. Weizel and U. Kulp, Ann. d. Physik **4**, 971 (1930). The analysis of the same system as given by these authors is based on seventeen heads measured by Walter and Barrat, Proc. Roy. Soc. **A119**, 257 (1928).

[3] W. R. Fredrickson and W. W. Watson, Phys. Rev. **30**, 429 (1927).

$$\nu = 15377.35 + 74.88(v' + \tfrac{1}{2}) - 0.30(v' + \tfrac{1}{2})^2 - 92.35(v'' + \tfrac{1}{2}) + 0.34(v'' + \tfrac{1}{2})^2 \quad (2)$$

The infrared system was first photographed by McLennan and Ainslee.[4] They gave the measurements of nine heads extending from λ8212 to λ8602. It is mainly with the latter system that this paper deals.

The region of the spectrum from λ6200 to λ8850 was photographed in the first order of a Rowland concave grating giving a dispersion of 2.632A per mm. The vapor was contained in a glass tube 80 cm long heated electrically. The source of light was a 150 watt lamp. In the process of this investigation the heads of the bands of the red system were measured in an attempt to obtain a more accurate equation.

Shortly after this work had begun Ritschl and Villars[5] published a short note on the vibrational analysis of the infrared system, $B^1\Sigma \leftarrow A^1\Sigma$, giving the following equation, as expressed in half quantum numbers:

$$\nu = 11584.9 + 71.43(v' + \tfrac{1}{2}) - 0.40(v' + \tfrac{1}{2})^2 - 91.40(v'' + \tfrac{1}{2}) + 0.30(v'' + \tfrac{1}{2})^2. \quad (3)$$

No data or measurements were given in that note and insofar as we know none were given subsequently. This equation has been tested by the authors and, as will be shown later, is probably incorrect.

RESULTS

Red system: In this system twenty six new heads were obtained bringing the total to seventy. These additional bands correspond to transitions involving higher quantum numbers than the bands measured by Fredrickson and Watson.[3] With the new measurements the following equation was obtained:

$$\nu = 15377.73 + 74.73(v' + \tfrac{1}{2}) - 0.327(v' + \tfrac{1}{2})^2 - 92.64(v'' + \tfrac{1}{2}) + 0.354(v'' + \tfrac{1}{2})^2 \quad (4)$$

The new equation is believed to be more accurate since it includes heads of higher quantum numbers than Eq. (2). Table I gives the wave-length and wave-number values for this system. The average observed minus calculated difference is 0.39 cm^{-1}.

Far red system: The far red system contains many more observable heads than the one discussed above. Also, the bands are less clearly differentiated due to the great amount of overlapping throughout the entire system. This overlapping is also responsible for the presence of many faint markings on the plates whose appearance does not show whether they are heads or accidental condensations of lines. In all, two hundred apparent heads have been measured. It is doubtful, however, whether or not all of these are actually heads.

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[4] J. C. McLennan and D. S. Ainslee, Proc. Roy. Soc. **A103,** 304 (1923).

[5] R. Ritschl and D. Villars, Naturwiss. **16,** 219 (1928).

TABLE I. *Near red system.*

$v'-v''$	$\lambda_{(\text{air})}$ (I.A.)	$\nu_{(\text{vac})}$ (cm^{-1})	O−C (cm^{-1})	$v'-v''$	$\lambda_{(\text{air})}$ (I.A.)	$\nu_{(\text{vac})}$ (cm^{-1})	O−C (cm^{-1})
11-20	6922.19	14442.31	−0.96	3- 2	6489.03	15406.37	+0.64
10-19	6916.82	14453.53	−0.69	1- 0	6473.91	15442.35	−0.36
9-18	6911.37	14464.93	−0.30	2- 0	6443.15	15516.08	−0.05
8-17	6906.18	14475.80	−0.48	4- 1	6421.26	15568.96	−0.11
7-16	6900.86	14486.96	−0.44	3- 0	6413.03	15588.14	−0.75
6-15	6895.51	14498.21	−0.36	5- 1	6391.61	15641.01	+0.48
5-14	6890.49	14508.74	−1.05	4- 0	6383.67	15660.65	−0.36
4-13	6884.76	14520.82	−0.24	8- 3	6379.80	15670.15	+0.93
9-17	6873.70	14544.18	−0.95	7- 2	6371.53	15690.00	−0.25
8-16	6867.93	14556.40	−0.49	6- 1	6363.22	15710.98	−0.35
7-15	6862.24	14568.47	−0.24	10- 4	6360.99	15716.48	+0.04
6-14	6856.87	14579.89	−0.70	5- 0	6354.55	15732.41	−0.05
5-13	6850.94	14592.55	+0.03	13- 6	6351.42	15740.17	+0.59
4-12	6845.41	14604.40	−0.10	8- 2	6343.33	15760.23	+0.49
9-16	6835.88	14624.67	−1.06	16- 8	6343.33	15760.23	+0.57
8-15	6829.49	14638.33	+0.12	12- 5	6342.19	15763.08	+0.33
7-14	6823.96	14650.00	−0.74	7- 1	6334.63	15781.89	+0.41
6-13	6817.79	14663.47	+0.15	15- 7	6334.63	15781.89	−0.49
5-12	6812.00	14675.93	−0.03	11- 4	6333.90	15783.71	−0.26
4-11	6805.91	14689.06	+0.41	6- 0	6325.99	15803.44	+0.17
3-10	6800.33	14701.13	−0.26	10- 3	6325.03	15805.84	−0.41
5-11	6773.47	14759.42	−0.69	14- 6	6325.03	15805.84	+0.69
4-10	6767.00	14773.52	+0.01	9- 2	6315.90	15828.68	+0.09
3- 9	6760.79	14787.28	+0.32	13- 5	6315.90	15828.68	+0.71
2- 8	6754.68	14800.46	−0.01	8- 1	6307.05	15850.88	−0.09
1- 7	6748.22	14814.64	+0.61	12- 4	6307.05	15850.88	+0.03
4- 9	6728.08	14859.00	−0.07	7- 0	6298.11	15873.40	−0.01
3- 8	6721.19	14874.24	+1.01	11- 3	6298.11	15873.40	−0.39
2- 7	6715.08	14887.75	+0.30	10- 2	6288.51	15897.63	+0.86
1- 6	6708.78	14801.73	+0.02	13- 4	6280.79	15917.16	+0.08
0- 5	6702.38	14815.97	−0.07				
3- 7	6682.39	14860.59	+0.36				
2- 6	6675.79	14875.37	+0.24				
1- 5	6669.22	14890.11	+0.02				
0- 4	6662.51	15005.23	+0.09				
1- 4	6629.84	15079.15	−0.06				
0- 3	6622.81	15095.16	+0.21				
4- 6	6611.62	15120.74	+0.73				
3- 5	6605.11	15135.61	−0.68				
0- 2	6583.37	15185.60	+0.13				
4- 5	6573.06	15209.42	+1.01				
2- 3	6558.45	15243.31	+0.86				
0- 1	6544.13	15276.67	−0.03				
2- 2	6520.02	15333.19	+0.23				
1- 1	6512.58	15350.66	−0.11				
0- 0	6505.08	15368.35	−0.29				

The first step in the investigation was to test the formula of Ritschl and Villars. It was found that a large number of heads could be fitted into this formula if it were modified slightly. It was noticed further that on the basis of the above equation the distribution of the bands within the system was somewhat erratic. The main objections to this formula however were two: (1) the value of ω_e'', (2) the heat of dissociation derived from their equation for the upper state.

It will be seen that ω_e'' of Eq. (3) differs somewhat from that of Eqs. (1) or (4). Ritschl and Villars did not state the number of heads from which Eq. (3) was derived, but it was thought that when a large number of heads were included into this system the discrepancy would disappear. Indeed, we have found that the ω_e'' obtained by us, in testing Eq. (3), was 91.92, a difference of 0.72 cm^{-1} from the ω_e'' of Eq. (4), as compared with 1.24 cm^{-1} resulting from the equation as given by Ritschl and Villars. When, however, the value of 92.64 was inserted into Eq. (3) it was found that the deviations were far greater than the experimental accuracy warranted. The heads of the infrared system actually did not fit this modified equation. An attempt was then made to account for the discrepancy by the fact that the theoretical equations are derived for band origins, while in both systems band heads had been used. However with any reasonable assumption as to distance of heads to origins the correction introduced is about 1/100 of the above discrepancy.[6]

The second objection to Eq. (3) is the calculated heat of dissociation of the upper state. It has been assumed that the lowest state of K_2, $A^1\Sigma$, dissociates into two normal potassium atoms, while the excited state, $C^1\Pi$, dissociates into a normal atom and an excited ^2P atom as illustrated in Fig. 1. Birge[7] using Eq. (2) calculated the heat of dissociation of the upper state as 0.57 volts. From this he derived the heat of dissociation for the lower state as 0.89 volts, by making use of the assumption noted above. Using the more accurate Eq. (4) we obtain for the upper state:

$$A^1\Pi:\ D' = \frac{(74.73)^2}{4 \times 0.327 \times 8106} = 0.527 \text{ volts} \tag{5}$$

and for the lower state:

$$A^1\Sigma:\ D'' = \frac{(92.64)^2}{4 \times 0.354 \times 8106} = 0.748 \text{ volts} \tag{6}$$

From Eq. (5) we obtain:

$$H_{\text{red}} = \frac{15377.73}{8106} + 0.527 = 2.424 \text{ volts} \tag{7}$$

where $H = \nu_e + D'$; ν_e being the electronic energy of the system involved and D' the heat of dissociation of the upper level of that system. D'' is not expected to be as accurate as D' since fewer levels are known for the lower state.

Reverting to Eq. (3) of Ritschl and Villars; the lower state of the infrared system is the same as that of the red system i.e., $A^1\Sigma$. Therefore we would expect the upper state to dissociate into one normal and one ^2P excited atom, or into a normal atom and an atom with higher excitatoin potential than the atomic ^2P state. Calculating D' from Eq. (3) we get:

$$D' = \frac{(71.40)^2}{4 \times 0.40 \times 8106} = 0.393 \text{ volts} \tag{8}$$

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[6] The values of ω_e'' as obtained independently from two different systems by Yamamoto and us agree to within 0.1 percent.

[7] International Critical Tables, **V**, 410–418 (1929).

The total energy is:

$$H_{\text{infrared}} = \frac{11584.9}{8106} + 0.393 = 1.822 \text{ volts} \tag{9}$$

as compared with 2.424 volts.

H, as derived from Eq. (9) is too small, and since the first excited state of *K* is the ^2P state, and there is no intermediate atomic state into which the molecule can dissociate the equation necessarily must be wrong. The difference, 0.608 volts, is almost twice as much as D' of Eq. (8) and although

TABLE II. *Far red system.*

$v'-v''$	$\lambda_{(\text{air})}$ (I.A.)	$\nu_{(\text{vac})}$ (cm^{-1})	O−C (cm^{-1})	$v'-v''$	$\lambda_{(\text{air})}$ (I.A.)	$\nu_{(\text{vac})}$ (cm^{-1})	O−C (cm^{-1})
0–4	8840.82	11308.06	+0.7	10–4	8342.49	11983.54	+1.9
4–7	8834.14	11316.60	−1.0	6–1	8339.84	11988.34	+1.2
3–6	8819.42	11335.54	+0.1	13–6	8331.28	12000.50	+0.2
2–5	8803.14	11355.84	+0.0	5–0	8321.93	12013.29	+1.5
0–3	8773.15	11395.28	−2.0	11–4	8298.35	12047.28	−0.0
4–6	8765.70	11404.97	+1.7	7–1	8294.79	12053.31	−0.8
3–5	8752.92	11421.62	−2.2	14–6	8286.48	12064.52	−0.6
2–4	8735.33	11444.61	−0.1	10–3	8280.21	12073.67	+1.3
6–7	8729.85	11451.81	+1.4	6–0	8275.42	12080.67	+1.6
1–3	8719.74	11465.13	−1.0	13–5	8270.51	12087.83	+0.1
0–2	8702.00	11488.46	+0.7	9–2	8206.70	12093.34	−2.4
4–5	8700.95	11489.85	−1.9	16–7	8259.44	12104.04	−2.1
1–2	8651.79	11555.20	+1.9	12–4	8255.02	12110.51	−2.7
5–5	8650.00	11557.52	−1.7	11–3	8237.91	12135.67	−1.4
0–1	8634.43	11578.41	−0.6	14–5	8226.85	12151.99	−1.5
4–4	8632.00	11581.60	+0.8	10–2	8220.09	12161.99	+0.1
8–7	8629.59	11584.82	+0.8	17–7	8214.24	12170.64	+0.6
3–3	8616.29	11602.74	−0.0	12–3	8192.50	12202.28	−0.2
2–2	8599.15	11625.66	−0.7	8–0	8186.45	12211.94	−0.8
6–5	8599.15	11625.66	−0.8	15–5	8181.49	12219.33	+1.3
1–1	8582.40	11647.80	0.0	11–2	8175.83	12227.80	+0.2
5–4	8582.40	11647.80	−0.5	18–7	8173.15	12231.83	−1.8
9–7	8580.66	11650.90	+0.6	21–9	8160.56	12250.70	+0.6
0–0	8566.30	11670.46	−0.1	20–8	8145.80	12272.90	−0.0
3–2	8549.89	11692.83	−0.4	19–7	8130.74	12295.64	−1.3
6–4	8533.51	11715.30	−0.3	15–4	8122.31	12308.39	+1.3
2–1	8532.50	11716.68	+0.4	11–1	8117.13	12316.26	−2.5
10–7	8532.50	11716.68	+0.3	17–6	8114.36	12320.45	−0.9
1–0	8515.75	11739.72	−0.0	14–3	8107.71	12331.55	−0.9
4–2	8499.51	11762.17	+1.1	16–4	8081.93	12369.90	−1.4
3–1	8483.08	11784.97	+0.5	23–9	8078.32	12375.41	+1.7
10–6	8468.23	11805.60	+1.5	12–1	8071.10	12384.00	−0.0
6–3	8468.23	11805.60	+0.2	19–6	8071.10	12384.00	−0.6
2–0	8468.23	11805.60	−2.6	22–8	8062.89	12399.09	+1.2
9–5	8453.60	11826.03	−0.4	11–0	8054.71	12412.69	+1.9
5–2	8450.75	11830.07	+1.4	20–6	8030.75	12448.77	+1.2
12–7	8438.04	11847.84	+0.3	13–1	8030.75	12448.77	−0.6
8–4	8438.04	11847.84	−1.4	19–5	8014.74	12473.59	+0.6
4–1	8434.47	11852.86	+0.6	21–6	7990.34	12512.48	+2.5
7–3	8419.99	11873.30	+1.0	14–1	7988.33	12514.77	+0.4
3–0	8418.25	11875.69	−0.7	24–8	7985.31	12519.57	−2.1
10–5	8405.84	11893.24	−0.7	17–3	7980.68	12526.84	+1.8
6–2	8403.55	11896.47	+0.6	27–10	7977.78	12531.36	−1.9
5–1	8387.83	11918.80	−1.1	13–0	7972.02	12540.43	+1.3
4–0	8370.62	11943.27	−0.9	23–7	7968.52	12545.97	−1.1
11–5	8359.85	11958.65	+0.4	16–2	7964.36	12552.50	+0.8
7–2	8358.61	11961.10	−1.8	26–9	7961.22	12557.44	−0.6

TABLE II. (*Continued*)

$v'-v''$	$\lambda_{(\mathrm{air})}$ (I.A.)	$\nu_{(\mathrm{vac})}$ (cm^{-1})	O−C (cm^{-1})
19– 4	7956.88	12564.29	+2.1
22– 6	7952.69	12570.88	−1.8
15– 1	7946.90	12579.80	+1.1
25– 8	7943.48	12585.33	+2.2
18– 3	7942.32	12587.32	−1.3
21– 5	7934.69	12599.57	+1.0
14– 0	7931.11	12605.13	−1.0
24– 7	7929.25	12608.08	−0.6
27– 9	7922.18	12619.21	+0.3
20– 4	7918.90	12625.00	−0.1
23– 6	7911.95	12635.65	+1.0
16– 1	7907.23	12643.18	+0.3
29–10	7900.78	12653.50	−0.5
22– 5	7895.46	12662.00	+1.0
25– 7	7890.22	12670.40	+0.3
24– 6	7873.70	12697.00	+0.6
27– 8	7868.48	12705.45	+0.3
17– 1	7866.53	12708.60	+1.8
29– 9	7848.54	12737.70	−1.9
28– 8	7831.28	12765.80	+0.2
18– 1	7829.07	12769.40	0.0
31–10	7827.66	12771.70	−1.8
20– 2	7807.20	12805.30	−0.1
23– 4	7803.10	12812.20	+0.1
26– 6	7798.83	12818.90	−0.1
29– 8	7793.90	12827.02	+1.1
31– 9	7774.18	12859.60	+0.5
18– 0	7772.80	12816.60	−0.7
21– 2	7768.96	12868.96	−0.0
29– 7	7732.60	12911.60	−1.2
32– 9	7728.30	12918.80	+0.4

the equation from which the heats of dissociation are obtained may be first approximations, we would not expect that the deviations would be so large.

The equation of Ritschl and Villars was therefore abandoned and combinations between the heads were sought so that the ω_e'' derived from this system would be the same, within experimental error, as those obtained from the blue and the red systems. Such combinations were found, resulting in a new analysis in which 119 heads were included. The equation connecting these heads is:

$$\nu = 11683.58 + 69.09(v' + \tfrac{1}{2}) - 0.153(v' + \tfrac{1}{2})^2 - 92.64(v'' + \tfrac{1}{2}) + 0.354(v'' + \tfrac{1}{2})^2 \qquad (10)$$

In this equation the origin and all the constants are different from those given by Ritschl and Villars. The average observed minus calculated value based on this equation is 0.93 cm.$^{-1}$. Table II gives the heads of the system and their assigned quantum numbers. The remaining 80 heads have been examined carefully and most of them are apparently accidental condensations of lines.

It is seen from Eq. (10) that the constants of the lower state are exactly the same as those of the red and blue systems.

HEATS OF DISSOCIATION

From the upper level of the red system we obtained $H_{\text{red}} = 2.424$ volts. Calculating D' from Eq. (10) we obtain:

$$B^1\Sigma: D' = \frac{(69.09)^2}{4 \times 0.153 \times 8106} = 0.962 \text{ volts} \qquad (11)$$

and

$$H_{\text{infrared}} = \frac{11683.58}{8106} + 0.964 = 2.402 \text{ volts.} \qquad (12)$$

The values of H as obtained from two different states agree within 1 percent.

From the blue system, we obtain:[8]

$$D' = \frac{(61.28)^2}{4 \times 0.24 \times 8106} = 0.483 \text{ volts} \qquad (13)$$

and

$$H_{\text{blue}} = \frac{22970.0}{8106} + 0.483 = 3.311 \text{ volts.} \qquad (14)$$

From the equation $H = \nu_{\text{e(mol)}} + D' = D'' + \nu_{\text{(atom)}}$
we obtain for the excitation potential of the atom $\nu_{\text{(atom)}}$:

$$\nu_{\text{(atom)}} = 3.31 - 0.81 = 2.50 \text{ volts} \qquad (15)$$

as compared with

$$5^2S - 4^2S = 2.596 \text{ volts}$$

$$4^2D - 4^2S = 2.658 \text{ volts.}$$

The last two values are within the experimental error involved in Eq. (15). It is probable, however, that the upper state of the blue system is also $^1\Sigma$, which upon dissociating gives a normal atom and a 5^2S atom.[9]

Taking H'' as the mean of the two values in Eqs. (7) and (12) i.e. 2.41 volts we find that[10]

$$D'' = 0.81 \text{ volts}$$

On the other hand, from the constants of the lower state we obtain:

$$D'' = 0.75 \text{ volts}$$

a difference of only 0.06 volts between the two values.

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[8] These are essentially the same values as given by Yamamoto.

[9] Professor Mulliken has pointed out that the lowest state of K_2, (cf. the corresponding state of Na_2), since it is a singlet state, must be $A^1\Sigma_g{}^+$. The first excited state is $B^1\Sigma_u$, the second $C^1\pi_u$ while the third is in all probability a $D^1\Sigma_u{}^+$. g (gerade) = even, u (ungerade) = odd, in the sense of these terms used by Hund.

[10] We have taken $4^2S - 4^2P$ of the K atom to be 1.608 volts.

In Figure 1 the four $U(r)$ curves for the states A, B, C, and D, are drawn using the formula given by Morse.[11] r_0 values were obtained by means of the equation given in the same paper, i.e. $\omega_0 r_0^3 = 3000 \times 10.^{-24}$

The heat of dissociation for the normal state of K_2 was obtained by Carelli and Pringsheim[12] from two somewhat similar methods, the values given by them being 0.63 volts and 0.53 volts. Somewhat later Ditchburn[13] calculated the heat of dissociation as 0.51 volts.

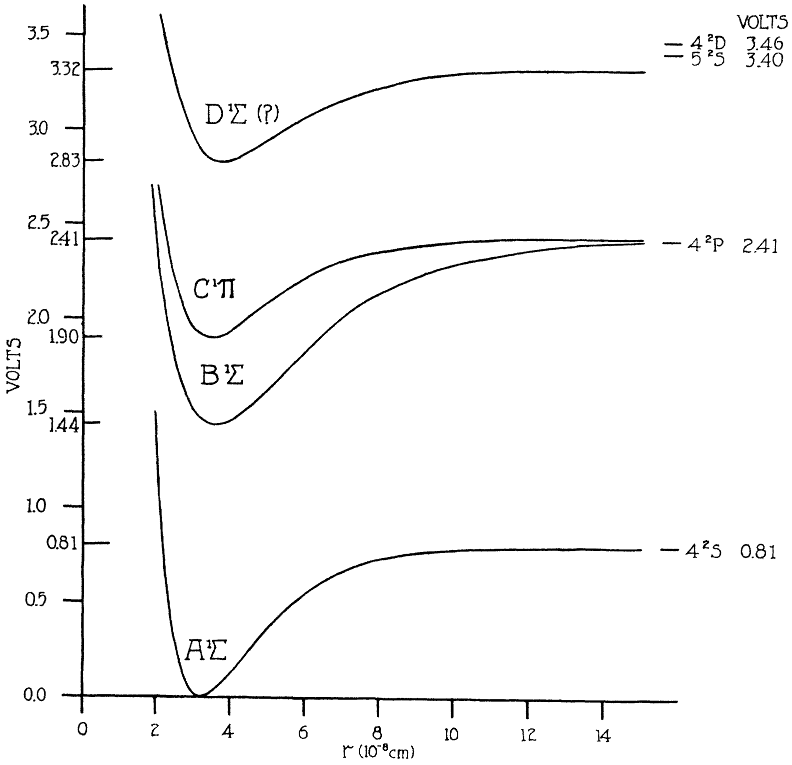

Fig. 1. $U(r)$ curves for the electronic states A, B, C and D.

In the experiment of Carelli and Pringsheim the vapor pressure of the molecules in thermodynamic equilibrium with the atoms was measured at several different temperatures. However the vapor pressure was not directly measured but was assumed to be proportional to the intensity of the band fluorescence produced when white light was passed through the vapor. The experimental errors involved in measuring the blackening of the plate etc. are rather large. Furthermore the heat of dissociation is obtained from the slope of the equation (first method, the second method is exactly analogous) log $(IT) = f(1/T)$, where I is the intensity of the band fluorescence and T

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[11] P. R. Morse, Phys. Rev. **34**, 61 (1929).

[12] A. Carelli and P. Pringsheim, Zeits. f. Physik **55**, 643 (1927).

[13] R. W. Ditchburn, Proc. Roy. Soc. **A117**, 486 (1928).

the absolute temperature. It can be shown easily that this method would not give an accurate value of the heat of dissociation. A very slight change in the slope of the line drawn through their points would give a totally different value for the heat of dissociation. The value 0.75 volts is within their experimental error, and it is actually obtained from one of the four curves given in their paper.[14]

In Ditchburn's experiment white light was passed through a tube containing potassium vapor and the wave-length of the maximum in the region of continuous absorption was found. Ditchburn finds a maximum absorption at about 5820A corresponding to 2.12 volts, and interprets this value as being the sum of the dissociation energy of the molecule in the lower state plus the energy required to excite the atom from the 4^2S to the 4^2P state. Since the latter energy is known accurately, he derives the dissociation energy of the molecule as $D''=0.5$ volts. The value obtained by him 2.12 volts, is to be compared with the mean value of H obtained from Eqs. (7) and (12), i.e. 2.41 volts. It should be noted that our value corresponds to a transition from the lowest vibrational state of A (refer to Fig. 1) to the threshold value of dissociation in the two upper states B and C, i.e. 2.41 volts corresponds to dissociation at $T=0°\text{K}$.

The position of the maximum in the continuum depends upon two factors, first, upon the number of molecules in the lower states from which by absorption of light a molecule dissociates, and second, upon the probability of such transitions. The first factor depends upon the temperature of the absorbing gas, while the second depends upon the shape of the $U(r)$ curves of the states involved, here A and C. It is seen from Fig. 1 that the maximum probability of transitions from A to the threshold value of C is from the vibrational level of A corresponding to an energy of 0.45 volts. However we would expect the number of molecules in this particular level to be less than that of lower vibrational states. Hence the maximum will occur for transitions arising from vibrational levels lower than 0.45 volts.[15] Ditchburn's value indicates that the maximum corresponds to transitions from the vibrational level of 0.3 volts. He does not give the temperature at which this experiment was performed, however we can see from Fig. 1 that in general heats of dissociation obtained by measuring the wave-lengths of the region of maximum absorption from states A to C will be too low.

It is with pleasure that the authors acknowledge their indebtedness to Professor W. W. Watson for suggesting this problem and to Professor R. S. Mulliken for his valuable criticism and advice.

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[14] Carelli and Pringsheim, Zeits. f. Physik **44,** 645, dotted line of Fig. 2.

[15] See discussion on transition probabilities by R. S. Mulliken, Rev. Modern Physics **2,** 78–83 (1930).