

## The Band Spectrum of NaK

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The spectrum of the NaK molecule has been studied in absorption and in magnetic rotation throughout the visible and photographic infrared regions. By means of magnetic rotation the upper vibrational levels of the orange system have been followed nearly to dissociation, permitting accurate determinations of the energies of dissociation of four states of the molecule, that of the ground state being  $0.62 \pm 0.03$  volt. Two new band systems, in the green and

infrared, have been found and analyzed. The fourth theoretically expected system has not been found and is presumably covered by strong Na<sub>2</sub> and K<sub>2</sub> systems. The magnetic rotation spectra in the green and red have no simple relation to the absorption spectra and are probably to be interpreted as due to perturbations, like the red magnetic rotation spectrum of Na<sub>2</sub>.

HITHERTO the only known visible band system of NaK has been the one in the neighborhood of the sodium *D*-lines.<sup>1</sup> There are, however, two visible systems of Na<sub>2</sub> and a visible and infrared system of K<sub>2</sub>, in each case involving transitions from a <sup>1</sup>Σ molecular ground level which dissociates into normal sodium, or potassium, atoms to excited molecular <sup>1</sup>Σ and <sup>1</sup>Π levels both of which dissociate into one normal atom and one in the resonance (<sup>2</sup>*P*) state. Theory indicates that there should be four systems of NaK bands in the visible and infrared, since, besides the ground level which dissociates into normal sodium and potassium atoms, there should be a pair of levels, <sup>1</sup>Σ and <sup>1</sup>Π, dissociating into normal sodium and excited potassium and a similar pair dissociating into normal potassium and excited sodium.

In the present investigation the apparatus used by Loomis and Nusbaum<sup>2</sup> for the study of the absorption and magnetic rotation spectra of Li<sub>2</sub>, Na<sub>2</sub> and K<sub>2</sub> has been used in a search for the three unknown band systems of NaK. Two of them have been found and their vibrational structure analyzed and, in addition, the previously known orange system has been extended far enough to yield an accurate value of the heat of dissociation.

The chief difficulty has been that the strong band systems of Na<sub>2</sub> and K<sub>2</sub> cover nearly the whole of the visible and infrared spectrum. It has been possible to overcome this to some extent by taking advantage of the fact that the concentra-

tions of the three molecules are respectively proportional to the products of the concentrations of their constituent atoms and by working with sodium with just a trace of potassium in the regions of the spectrum where the potassium bands, or lines, were troublesome and *vice versa*. As a consequence, it has been necessary to select, with considerable care, for each of many rather narrow spectral regions, the appropriate concentration, temperature, exposure, spectrograph and type of photographic plate. The concentration of either constituent cannot be decreased indefinitely by the above method because the total pressure eventually becomes so high as to cause troublesome broadening of the band lines.

The spectra were studied over the range 4500–11,500Å, with the use, for the longer wavelengths, of the new Eastman Q type plates.

The constants of the levels concerned in these systems are given in Table I. The infrared, orange and green systems are transitions from the ground state (*G*) to the excited levels *A*, *C* and *D*, respectively. The bands which we earlier<sup>3</sup> erroneously reported as constituting the fourth system have since been found to be merely the part of the infrared (*A*←*G*) system which lies to the high frequency side of the potassium resonance lines. The constants  $T_e$ ,  $\omega_e$ ,  $x_e\omega_e$ ,  $y_e\omega_e$ ,  $z_e\omega_e$  in Table I are those in the usual expansion

$$T(v) = T_e + \omega_e(v+1/2) - x_e\omega_e(v+1/2)^2 + y_e\omega_e(v+1/2)^3 + z_e\omega_e(v+1/2)^4 \dots \quad (1)$$

<sup>1</sup> Ritschl and Villars, *Naturwiss.* **16**, 219 (1928).

<sup>2</sup> Loomis and Nusbaum, *Phys. Rev.* **38**, 1447 (1931); **40**, 380 (1932); **39**, 89 (1932).

<sup>3</sup> Loomis and Arvin, *Phys. Rev.* **44**, 126 (1933).

TABLE I. Constants of the various levels for NaK.

State	$T_e$	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$D_e$ volts	Dissociation products	Type
G	0	123.29	+0.400			0.62	Na+K	$^1\Sigma^+$
D	20,090.55	82.17	+0.350	-0.00814		0.24	Na'+K	$^1\Pi$
C	16,991.37	72.60	+1.475	+0.02436	-0.000545	0.14	Na+K'	$^1\Pi$
B	Not found						Na'+K	$^1\Sigma^+$
A	12,139.65	79.852	+0.0872	-0.003887		0.74	Na+K'	$^1\Sigma^+$

TABLE II. Frequencies of absorption bands of the green system.

$v',v''$	Intensity	Obs.	Obs.- Calc.	$v',v''$	Intensity	Obs.	Obs.- Calc.	$v',v''$	Intensity	Obs.	Obs.- Calc.
0,10	0	18882.0	+0.9	2,2	3	19987.2	-0.7	8,0	1	20697.3	+0.1
0,9	1	18999.5	+3.1	4,3	3	20025.4	-0.4	12,2	1	20744.7	+3.3
0,8	3	19113.8	+1.3	3,2	1	20066.3	-1.5	9,0	1	20771.3	+0.2
0,7	5	19229.6	+0.2		1	20079.1		15,3	0	20820.6	-2.6
3,9	1	19240.4	+2.0	2,1	1	20109.2	-0.4	10,0	1	20844.0	+0.2
1,7	2	19310.8	-0.1	4,2	2	20145.3	-1.4	16,3	1	20889.7	+1.8
		19329.9		9,5	2	20168.3	+1.7	11,0	1	20915.7	+0.4
0,6	5	19346.1	-1.0	4,1	2	20269.7	+1.3	13,1	0	20930.0	-2.0
1,6	3	19428.8	+0.2	3,0	2	20315.6	+3.6	17,3	0	20953.3	+2.2
0,5	3	19463.7	-1.8	8,3	0	20329.1	-3.0	12,0	0	20984.4	-1.2
1,5	3	19545.7	-1.3	5,1	2	20346.2	-0.4	14,1	0	20999.0	-0.6
0,4	1	19581.3	-3.7	6,1	2	20426.2	+2.6	16,2	0	21010.3	+1.5
1,4	3	19665.4	-0.9		1	20461.5		13,0	1	21053.3	-1.2
2,4	5	19744.1	-2.8	7,1	1	20499.4	-0.3	14,0	1	21121.7	-0.4
	1	19773.5		9,2	1	20525.5	-1.4	16,1	0	21129.8	-0.7
1,3	5	19785.8	-0.6	6,0	1	20545.5	-0.6	15,0	0	21191.4	+3.1
2,3	3	19865.4	-1.6		1	20605.5		17,1	0	21191.4	-2.3
3,3	3	19947.3	+0.4	7,0	1	20623.6	+1.4	16,0	1	21253.1	+0.1
	1	19954.5		9,1	1	20648.7	+0.1	17,0	0	21313.5	-2.7
	2	19964.7		11,2	1	20670.7	-0.4				

for the vibrational energy of a diatomic molecule.  $D_e$  represents the energy of dissociation of the particular state, in volts, from the equilibrium energy for that state; all the others are based on the extrapolation of the C state, which is believed to be the most accurate.

Tables II, III and IV give the frequencies of all band heads measured, in the green, orange and infrared systems, respectively, with the quantum numbers assigned to them and the differences between the frequencies observed and those calculated from the differences of the terms in Eq. (1) with the constants in Table I. The intensities reported are rough visual estimates. In each system the assignments become dubious near the short wave-length end, due to overlapping.

The extrapolations of the A, C and D levels to dissociation are shown in Figs. 1, 2 and 3, respectively. The full curves represent the values calculated from Eq. (1) and the constants of Table I. The dashed curve in Fig. 2 represents what appears to be the best extrapolation of the C level, based on the magnetic rotation measurements. The energy of the products of dissociation,  $(T_d)_C$ , so estimated, relative to the equilibrium

energy of the ground state, is  $18,087 \text{ cm}^{-1}$ . It is apparent from Fig. 2 that this figure can hardly be in error by more than  $250 \text{ cm}^{-1}$  or, say, 0.03 volt. Now the D levels have been followed as far as  $21,313 \text{ cm}^{-1}$ , and converge somewhat above this, say at  $22,000 \pm 400 \text{ cm}^{-1}$ , so the products of dissociation must be different from those of the C levels and, in fact, the excess of energy, so estimated,  $(T_d)_D - (T_d)_C = 3913 \pm 400 \text{ cm}^{-1}$  is about equal to the difference of

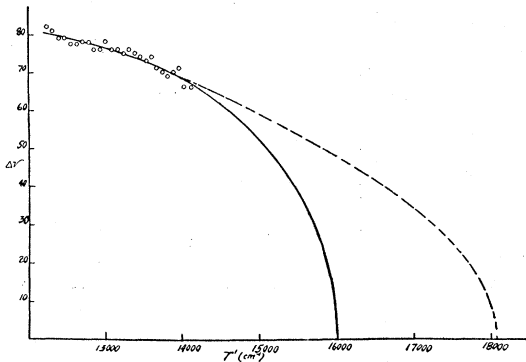


FIG. 1. Extrapolation of the A level to convergence. The full curve represents Eq. (1) and data in Table I. The dashed curve is an extrapolation consistent with that of the C level.

TABLE III. Frequencies of the magnetic rotation spectrum of the orange system.

$v',v''$	Intensity	Observed	Obs.-Calc.	$v',v''$	Intensity	Observed	Obs.-Calc.	$v',v''$	Intensity	Observed	Obs.-Calc.
18,0	0	17858.61	+0.27	7,0	8	17399.73	-0.13	16,6	10	17071.83	-0.27
	0	17838.65		12,2	2	17395.85	-0.97		15	17068.60	
22,1	0	17833.44	+1.76	25,5	2	17395.85	-5.10	10,4	*20	17065.25	-0.60
	0	17825.76			2	17388.34			20	17061.28	
	0	17818.14		24,5	0	17380.18	-0.18	0,1	15	16844.11	+0.85
21,1	0	17811.10	-0.63	9,1	0	17380.18	-0.11		10	16837.42	
	0	17805.96			1	17374.99			10	16834.33	
16,0	0	17797.14	+2.10	18,4	1	17371.55	-1.63		10	16829.46	
	0	17793.86		23,5	0	17364.93	-1.56		12	16825.32	
	0	17786.02		14,3	1	17356.79	-0.60		8	16811.20	
15,0	0	17759.86	+0.06	11,2	0	17351.44	-1.47		8	16807.70	
25,2	0	17755.12	+4.09	22,5	0	17351.44	+1.72	5,4	6	16805.50	+2.66
	0	17748.18		6,0	4	17345.22	+0.15	3,3	8	16797.48	-4.25
24,2	1	17742.14	+1.54	17,4	1	17345.22	+2.48	1,2	8	16789.85	-1.44
18,1	0	17736.06	+0.21		1	17335.34			3	16782.36	
	0	17727.31	+0.55	8,1	0	17329.29	-0.64		3	16771.07	
14,0	0	17723.15	+0.69	21,5	0	17329.29	-0.48		3	16757.81	
	1	17719.48			1	17320.45		4,4	3	16741.79	-1.68
	1	17714.10		13,3	1	17316.25	-1.51	6,5	3	16740.36	-0.26
22,2	1	17710.59	+0.59	10,2	3	17307.39	+0.56	2,3	3	16736.55	-0.83
17,1	1	17705.00	-0.41		4	17297.57		0,2	3	16720.79	-0.78
	1	17701.24			8	17288.19	+0.19		3	16717.30	
21,2	1	17689.46	-0.58	19,5	3	17282.38	+0.53		3	16714.21	
13,0	2	17683.57	+0.74	7,1	1	17277.74	+0.37		3	16706.40	
16,1	2	17672.78	+0.23	25,6	0	17277.74	+5.48		4	16703.22	
20,2	0	17668.89	+1.57	15,4	1	17272.14	-2.50		1	16699.85	
	1	17655.78			1	17266.07			1	16694.87	
12,0	3	17640.15	-0.85	24,6	1	17260.81	-1.02		1	16689.71	
19,2	1	17641.92	-0.20	9,2	1	17260.81	+2.21	5,5	1	16686.70	+3.15
15,1	1	17638.88	+1.57	18,5	1	17254.99	+1.10	3,4	2	16680.55	-1.09
25,3	1	17635.76	+5.63	23,6	1	17246.97	-1.03	1,3	6	16670.08	-0.32
	1	17626.63			1	17243.26			2	16654.60	
24,3	0	17618.65	-1.05	14,4	2	17236.27	-1.03		1	16641.67	
18,2	1	17612.98	-1.18	11,3	8	17231.18	-0.84		1	16629.37	
23,3	0	17607.43	+1.56	22,6	0	17231.18	-0.05	4,5	2	16623.64	-0.54
14,1	3	17601.21	+1.24	4,0	4	17228.87	+0.24	6,6	2	16623.64	+1.51
11,0	3	17597.63	+0.54	17,5	2	17225.00	+1.55	2,4	0	16617.01	-0.28
22,3	1	17589.43	+0.33	6,1	3	17221.82	-0.76		0	16613.12	
17,2	1	17585.13	+1.41		3	17218.30		0,3	8	16600.75	+0.07
	1	17580.68		21,6	0	17212.20	+0.92		0	16580.08	
	3	17577.61		8,2	2	17207.65	-0.59		0	16567.50	
21,3	2	17567.68	-1.47		1	17203.39		5,6	0	16565.46	+0.40
13,1	2	17560.22	-0.12		1	17201.00		3,5	1	16560.97	-1.38
10,0	3	17550.90	-0.11	13,4	1	17196.90	-0.77	1,4	3	16549.91	-0.40
16,2	1	17551.18	-0.32		1	17193.54			3	16544.74	
20,3	2	17545.78	-0.65	16,5	1	17190.95	+0.36		1	16532.90	
	0	17539.95		20,6	1	17190.95	+2.39		2	16528.22	
	1	17553.90			10	17181.57			2	16520.45	
	1	17528.96			3	17175.87		4,6	1	16507.95	+2.26
19,3	0	17521.95	+0.72	26,7	3	17170.59	+9.15	6,7	1	16501.40	-3.04
12,1	2	17518.38	-0.13	3,0	8	17166.20	-0.60	2,5	1	16496.89	-1.11
15,2	0	17515.84	+0.22	5,1	5	17164.78	-0.73		1	16493.29	
25,4	2	17512.17	+2.13	19,6	1	17164.78	+1.42	0,4	10	16480.27	-0.32
	3	17510.37		25,7	3	17159.82	+5.25		1	16465.49	
9,0	5	17502.71	-0.07	7,2	3	17157.17	+1.49		0	16458.33	
24,4	2	17500.32	+0.71		1	17151.27		5,7	0	16449.74	+2.47
	0	17497.71			3	17148.53		3,6	1	16443.07	-0.79
18,3	0	17491.61	-1.66	24,7	2	17142.05	-2.09		0	16439.19	
23,4	1	17486.30	+0.52	18,6	3	17135.71	+0.31		1	16434.89	
	0	17483.98		23,7	1	17131.57	+1.26	1,5	1	16430.41	-0.61
14,2	1	17477.83	-0.46		2	17128.82			0	16418.20	
22,4	0	17470.92	+1.91		3	17126.00			1	16405.05	
17,3	0	17465.75	+2.92		3	17120.93			1	16400.56	
	0	17462.64		14,5	6	17118.26	+0.25		1	16394.19	
8,0	4	17458.01		22,7	6	17113.45	-0.09	4,7	0	16387.81	-0.19
21,4	2	17452.45	+0.03	11,4	6	17109.97	-1.96	6,8	1	16387.81	+0.26
	0	17445.60	-3.46	4,1	15	17105.81	-0.33	2,6	4	16379.23	-0.28
	0	17440.62		2,0	10	17102.68	+0.23		8	16373.45	
13,2	1	17438.70	+0.05	6,2	4	17102.68	+1.79	0,5	8	16361.41	+0.11
16,3	0	17432.44	+2.47		4	17093.97			0	16344.63	
10,1	1	17427.94	-0.58		5	17092.12		1,6	0	16312.40	-0.13
20,4	0	17424.94	-1.40		5	17090.75			0	16306.39	
	0	17413.50		8,3	8	17086.93	-0.43		0	16293.60	
	0	17406.73			10	17082.28		0,6	3	16243.29	+0.48
19,4	4	17400.54	-0.60	13,5	10	17078.78	+0.40				

\* Estimates of intensities in the vicinity of the D-lines are unreliable.

TABLE IV. Frequencies of the absorption bands of the infrared system of NaK.

$v',v''$	Intensity	Observed	Obs.-Calc.	$v',v''$	Intensity	Obs.	Obs.-Calc.	$v',v''$	Intensity	Observed	Obs.-Calc.
0,10	3	10931	+2.9	9,3	1	12459	-1.4		3	13335	
0,9	4	11041	-3.4	6,1	1	12472	+2.1		2	13344	
1,9	1	11126	+1.9	11,4	1	12490		16,0	3	13356	+1.5
0,8	5	11158	-2.5	8,2	2	12504	0.0		1	13364	
1,8	1	11241	+0.8	7,1	3	12546	-1.8	18,1	0	13378	-0.5
0,7	3	11274	-3.4	6,0	1	12594	+1.6		3	13384	
1,7	1	11356	-1.1	11,3	2	12614	+0.1	25,5	1	13392	+3.3
0,6	1	11391	-4.0	8,1	2	12626	+0.3		1	13398	
1,6	1	11472	-2.7		2	12631		20,2	1	13400	-0.7
0,5	1	11512	-1.5		1	12636			3	13412	
1,5	1	11594	+0.8	10,2	1	12656	-2.2	22,3	0	13421	-0.3
2,5	1	11672	-0.6	7,0	2	12670	-0.4	17,0	3	13428	+0.0
1,4	4	11714	+1.5	9,1	0	12705	+2.0	24,4	0	13441	+1.2
2,4	4	11793	+1.1	14,4	0	12721	+0.4	19,1	2	13455	+4.0
4,5	1	11830	-0.9	11,2	3	12734	-0.8		1	13462	
1,3	0	11835	+2.4	8,0	2	12749	+0.8		1	13469	
3,4	3	11873	+1.9	10,1	0	12780	+0.1	21,2	1	13474.0	+2.2
2,3	5	11912	+0.1	15,4	1	12795	-0.2	23,3	2	13490	+0.9
1,2	3	11954	+0.5	12,2	1	12810	-0.9	18,0	3	13503	+2.0
3,3	10	11990	-1.0	9,0	1	12828	+2.5	20,1	1	13525	+2.6
5,4	1	12026	-2.8	14,3	0	12840	-0.7	22,2	2	13543	+0.8
2,2	5	12034	+1.1	11,1	2	12856	+0.5		1	13548	
4,3	5	12072	+1.7	13,2	0	12887	+0.6		1	13570	
3,2	5	12113	+0.9	18,5	0	12893	-3.5	19,0	2	13577	+3.8
5,3	2	12151	+2.1	10,0	3	12903	+0.6	21,1	1	13593	-0.5
2,1	1	12155	+0.4	12,1	1	12930	-2.6	25,3	3	13626	-2.0
7,4	0	12187	+1.8	16,2	1	13112	+1.7	20,0	0	13648	+3.1
4,2	5	12192	+0.8	13,0	2	13130	-0.6	22,1	0	13665	+1.1
3,1	2	12232	-1.8	18,3	1	13136	+0.1	26,3	1	13697	+1.5
11,6	1	12257	+1.0	15,1	1	13159	+1.1	21,0	0	13718	+2.0
8,4	1	12263	0.0	17,2	2	13182	-1.8	23,1	1	13735	+1.5
5,2	1	12268	-1.8	14,0	3	13205	-0.8	25,2	1	13750	+1.0
2,0	0	12275	-2.1	16,1	1	13233	+1.0	22,0	1	13790	+3.6
7,3	0	12306	+0.7	23,5	2	13251	-0.5		1	13797	
4,1	2	12315	+2.1	18,2	1	13258	+1.2	24,1	1	13806	+3.5
6,2	2	12348	+0.2	15,0	3	13281	+0.6	16,2	0	13816	-0.4
5,1	3	12392	+0.5	17,1	2	13308	-2.5		1	13829	
10,4	0	12418	+0.8	24,5	0	13322	+1.5	25,1	0	13872	+1.3
7,2	0	12424	-2.2	19,2	1	13329	0.0				

the frequencies of the resonance doublets of sodium and potassium,  $3951\text{ cm}^{-1}$ , so that it is natural to conclude that the  $C$  level dissociates into normal ( $3^2S$ ) sodium and excited ( $4^2P$ ) potassium and that the  $D$  level dissociates into normal ( $4^2S$ ) potassium and excited ( $3^2P$ ) sodium,<sup>4</sup> as stated in Table I. Assuming that the ground state of the molecule dissociates into normal atoms, as in  $\text{Li}_2$ ,  $\text{Na}_2$  and  $\text{K}_2$ , the energy of dissociation of the ground state

$$D_e'' = (T_d)_G = (T_d)_C - 13,015\text{ cm}^{-1} \\ = 5072\text{ cm}^{-1} = 0.62\text{ volt},$$

where  $13,015\text{ cm}^{-1}$  is the average frequency of the resonance doublet of potassium. This is verified, well enough to confirm the above conclusions as to products of dissociation, by a direct extrapolation of the vibrational levels of the ground state. It will be noted that this

<sup>4</sup> Calculations by Margenau, Phys. Rev. **40**, 398 (1932), indicate that at distances of approach greater than 5 or 6A, the forces of interaction between an excited ( $3^2P$ ) Na atom and a normal ( $4^2S$ ) K atom are repulsive. The existence of the stable  $D$  state clearly shows that at smaller distances, at which the equations of Margenau should not be expected to hold, this repulsion is overcome by ordinary valence forces.

value is, as expected, intermediate between the heats of dissociation of  $\text{Na}_2$  and  $\text{K}_2$  which are 0.76 and 0.51 volt, respectively. The most precise value of the energy of dissociation of the  $D$  state can then be obtained by

$$(T_d)_D = (T_d)_G + 16,966\text{ cm}^{-1} = 22,038\text{ cm}^{-1},$$

where  $16,966\text{ cm}^{-1}$  is the average frequency of the sodium resonance doublet. It is to this point that the dashed curve in Fig. 3 is extrapolated. The extrapolation of the  $A$  levels is long and dubious but if it is assumed that the products of dissociation are normal sodium and excited potassium, as stated in Table I, the energy of dissociation  $(T_d)_A$  must be the same as  $(T_d)_C = 18,087\text{ cm}^{-1}$ . The dashed curve in Fig. 1 is drawn to this point. It will be seen that this extrapolation is at least plausible. This is not true of an attempt to extrapolate this level to  $(T_d)_D = 22,038\text{ cm}^{-1}$ . Moreover this assignment accords better with the non-appearance of the fourth system. If the assignment in Table I is correct the  $B$  level may be expected to lie a little above the  $A$  level and the  $B \leftarrow G$  system will be covered by the infrared systems of both  $\text{Na}_2$

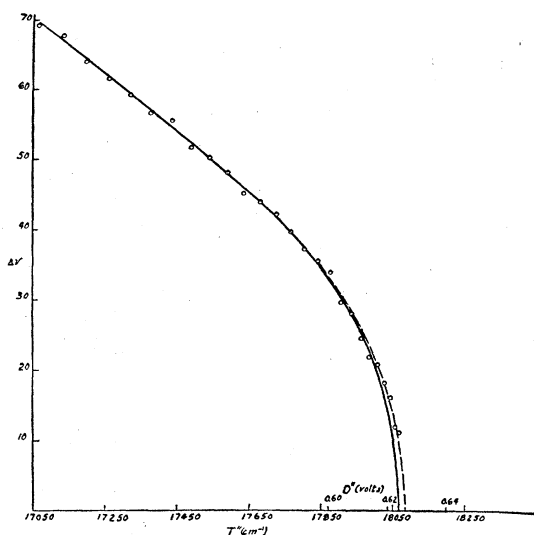


FIG. 2. Extrapolation of the C level to convergence. The full curve represents Eq. (1) and data in Table I. The dashed curve is the best extrapolation of the points.

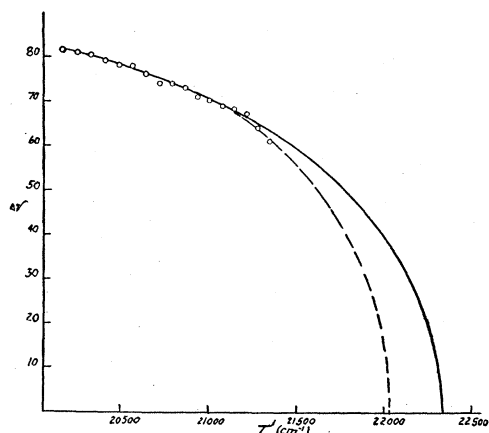


FIG. 3. Extrapolation of the D level to convergence. The full curve represents Eq. (1) and the data in Table I. The dashed curve is an extrapolation consistent with that of the C level.

and  $K_2$  and by the  $A \leftarrow G$  system of NaK. If the assignment were incorrect, the  $B \leftarrow G$  system should lie on the long wave side of the  $A \leftarrow G$  system and should have been observed.

With the apparatus of Loomis and Nusbaum,<sup>2</sup> magnetic rotation spectra have been observed in the region of each of the three absorption systems. The frequencies of the principal magnetic rotation lines of the orange system coincide approximately with those of the absorption band heads, just as do those in the  ${}^1\Pi \leftarrow {}^1\Sigma$

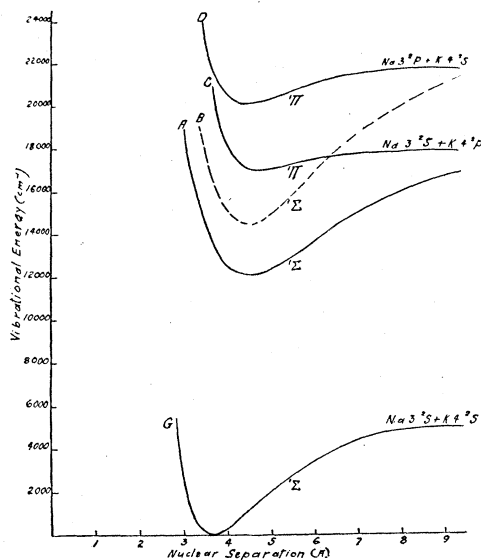


FIG. 4. Potential energy curves. That for the B state is hypothetical.

systems of lithium, sodium and potassium; and this analogy, together with the location of the origin of the system, indicates that the C state is  ${}^1\Pi$ . The measured frequencies of those magnetic rotation lines to which quantum numbers could be assigned are included in Table III, together with roughly estimated intensities. It will be observed that, as with  $Li_2$ ,  $Na_2$  and  $K_2$ , it has been possible to extend these assignments to higher values of  $v'$  than in absorption and the accuracy of the extrapolation to dissociation results chiefly from these measurements.

The magnetic rotation spectra in the regions of the green and infrared systems appear to resemble that of the red system of sodium. That is, although an interval approximately equal to the vibrational interval of the ground state is apparent on superficial inspection, nevertheless it is not possible to find any simple correspondence between the absorption and magnetic rotation spectra. An interpretation of this red magnetic rotation of sodium has been given by Fredrickson and Stannard,<sup>5</sup> to the effect that it is due to perturbations of the upper  ${}^1\Sigma$  state by an unknown  ${}^3\Pi$  state, which shares with the  ${}^1\Sigma$  state some of its magnetic properties. Presumably this interpretation can also be applied

<sup>5</sup> Fredrickson and Stannard, Phys. Rev. **44**, 632 (1933).

to the infrared magnetic rotation spectrum of NaK, which also lies in the region of a  ${}^1\Sigma \leftarrow {}^1\Sigma$  system; and also to the infrared magnetic rotation spectrum of  $K_2$ , which has been found incidentally to the work here reported. It is a little surprising, however, to have to call on the same hypothesis to account for the green magnetic rotation spectrum of NaK, since the upper level concerned in the green absorption system can, by analogy with  $Li_2$ ,  $Na_2$  and  $K_2$ , be hardly other than  ${}^1\Pi$ . It is true, however, that even in the green magnetic rotation system of  $Na_2$  there are many lines, including all those with what Wood<sup>6</sup> has called the positive direction of rotation, which do not fit into the vibrational analysis, nor correspond to absorption heads. One can suppose that these are also of the perturbation type; and one can then account for the non-appearance of a regular magnetic rotation spectrum of NaK in the green system by supposing that it is masked by a perturbation type of magnetic rotation which, for some reason, is considerably stronger.

Fig. 4 is a set of potential energy curves for the levels concerned in the above spectra, together with a dashed curve indicating the existence of the hypothetical  $B$  level. The curves are calculated according to the Morse formula, by using the values of  $\omega_e$  and  $D_e$  in Table I and, for want of measurements on rotational structure, taking the values of  $r_e$  from Badger's<sup>7</sup> recently published empirical formula in which  $d_{34}$  for NaK has been given the value 1.20 obtained by interpolating between  $d_{33}(Na_2) = 1.05\text{\AA}$  and  $d_{44}(K_2) = 1.35\text{\AA}$ .

Fig. 5 is an improved<sup>8</sup> Franck-Condon diagram for the three systems, in which  $T''$  is plotted as abscissa and  $T'$  as ordinate, downwards. The

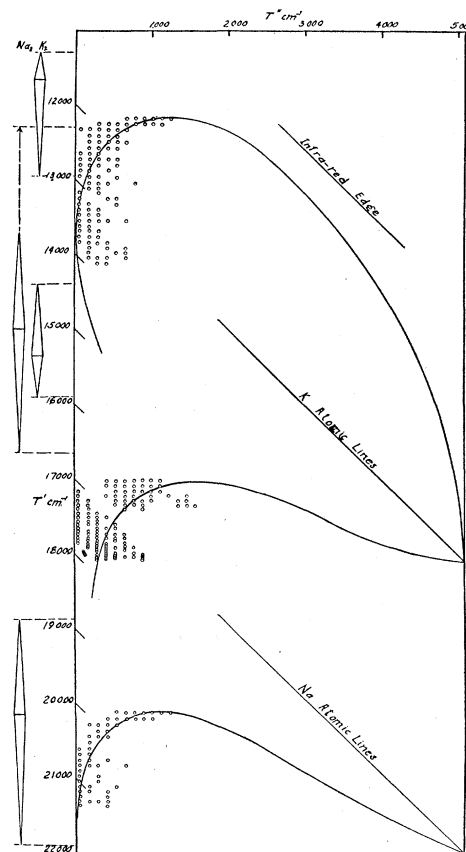


FIG. 5. Improved Franck-Condon diagram for the three systems. Overlapping systems of  $Na_2$  and  $K_2$  are schematically indicated in the left margin.

frequency of each band head can be found by projecting at  $45^\circ$  to the left and upwards on to the  $T'$  axis. The frequencies of the overlapping  $Na_2$  and  $K_2$  systems are schematically indicated on the margin. The curves are the theoretical loci of maximum intensity obtained in the usual way from the potential energy curves of Fig. 4. The long wave-length edge to the infrared system which, according to the theoretical curve should lie at  $10,150\text{ cm}^{-1}$  is actually found at  $9600\text{ cm}^{-1}$ .

<sup>6</sup> Wood, Proc. Am. Acad. **42**, 235 (1906); Astrophys. J. **30**, 339 (1909).

<sup>7</sup> Badger, J. Chem. Phys. **2**, 128 (1934).

<sup>8</sup> Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931).