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Magnetic Rotation Spectrum and Heat of Dissociation of the Sodium Molecule

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Wood's magnetic rotation spectrum of Na_2 had been extended by the method previously used with Li_2 and K_2, to higher vibrational levels. This leaves a very short extrapolation to dissociation. The energy of dissociation of the normal molecule, is $D_0=0.76\pm0.02$ volt, which is in good agreement with the best chemical data.

SEVERAL years ago the data on the green magnetic rotation spectrum of sodium as reported by R. W. Wood[1] were used by one of us[2] as a basis for a vibrational analysis of the band system and an estimate, by extrapolation, of the heat of dissociation of the normal Na_2 molecule. The result was given as 1.0 ± 0.1 volt. Since that time there has been an accumulation of chemical evidence that this figure is too high. Moreover a number of instances are now known in which the Birge-Sponer method of extrapolation has yielded misleading results, and the confidence in results like the above, which was based on such an extrapolation, has tended to diminish. Consequently the authors have thought it worthwhile to make new measurements on the magnetic rotation spectrum of sodium with a view to extending the levels observed as near dissociation as possible and thus increasing the accuracy of the result.

The apparatus previously used with Li_2 and K_2 was avilable and had been designed with just this purpose. That is, a long column of vapor was used, which brought out the weak lines corresponding to the highly excited levels near dissociation. For a description of the apparatus the reader is referred to previous papers.[3]

The magnetic rotation spectrum of sodium, as we observed it, did not extend appreciably further to the blue than Wood's did, but we were able because of the long path to measure a large number of faint bands in the short wave part of the region covered by Wood and these bands turned out to be the ones with high values of v' which we were seeking. In this way the series of observed upper vibrational levels, on which the accurate extrapolation to dissociation depends, has been extended from $v'=16$, the highest level identified in Wood's data, to $v'=26$, which, as appears below, represents an approach from within 0.13 volt of dissociation to within about 0.02 volt of it.

Table I gives all the bands which have been observed in the region of the plate which was measured. It was not thought worthwhile to extend measurements towards the red. The bands which had previously been reported by

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[1] Wood, Proc. Am. Acad. **42,** 235 (1906); Astrophys. J. **30,** 339 (1909).
[2] Loomis, Phys. Rev. **31,** 323 (1928).
[3] Loomis and Nusbaum, Phys. Rev. **38,** 1447 (1931) and **39,** 89 (1932).

TABLE I. *List of frequencies of all bands measured.*

v'	v''	Intensity	Frequency (cm^{-1})		Observed-Calculated
			Observed	Calculated	
23	5	1	21904.87	21906.31	−1.44
25	6	1	21904.87	21908.15	−3.28
21	4	1	21894.48	21895.68	−1.20
19	3	1	21876.09	21876.70	−0.61
14	0	1	21876.09	21874.64	1.45
17	2	1	21850.09	21849.80	0.29
24	6	1	21832.69	21833.44	−0.75
22	5	2	21826.45	21826.38	0.07
26	7	1	21823.29	21830.65	−7.36
15	1	1	21816.54	21815.43	1.11
20	4	1	21811.50	21810.75	0.75
18	3	1	21787.16	21787.00	0.16
13	0	1	21771.89	21774.01	−2.12
25	7	3	21756.25	21759.49	−3.24
16	2	3	21756.25	21755.56	0.69
21	5	1	21743.59	21743.92	−0.33
19	4	2	21722.40	21723.41	−1.01
14	1	2	21717.32	21716.87	0.45
17	3	6	21695.15	21695.00	0.15
24	7	3	21682.68	21684.78	−2.10
26	8	2	21675.99	21683.55	−7.56
22	6	2	21675.99	21676.15	−0.16
12	0	0	21670.07	21671.35	−1.28
15	2	6*	21659.05	21659.14	−0.09
20	5	6	21659.05	21658.99	0.06
18	4	4	21634.08	21633.71	0.37
25	8	0	21609.48	21612.39	−2.91
23	7	0	21606.62	21607.42	−0.80
16	3	2*	21601.93	21600.76	1.17
21	6	2	21593.87	21593.69	0.18
19	5	8	21572.35	21571.65	0.70
11	0	0	21565.22	21566.74	−1.52
14	2	3*	21560.10	21560.58	−0.48
17	4	2	21541.87	21541.71	0.16
26	9	0	21529.25	21538.05	−8.80
22	7	1	21526.37	21527.49	−1.12
12	1	2	21513.71	21513.58	0.13
15	3	10*	21504.04	21504.34	−0.30
18	5	4	21481.99	21481.95	0.04
25	9	0	21463.88	21466.89	−3.01
23	8	10	21459.71	21460.32	−0.61
10	0	10	21459.71	21460.21	−0.50
13	2	10	21459.71	21459.95	−0.24
16	4	3*	21447.46	21447.83	−0.37
21	7	0	21445.26	21445.03	0.23
19	6	1	21421.26	21421.42	−0.16
14	3	10*	21405.11	21405.78	−0.67
24	9	4	21390.66	21392.18	−1.52
17	5	4	21390.66	21389.95	0.71
26	10	2	21387.91	21394.15	−6.24
22	8	2	21381.38	21380.39	0.99
20	7	1	21359.70	21360.10	−0.40
12	2	2*	21356.88	21357.29	−0.41
9	0	5	21351.14	21351.84	−0.70
18	6	2	21332.14	21331.72	0.42
25	10	1	21320.32	21322.99	−2.67
23	9	1	21315.14	21314.82	0.32
13	3	10*	21305.17	21303.14	0.03
10	1	8	21302.11	21302.44	−0.33
16	5	8	21295.70	21295.71	−0.01
19	7	2	21272.46	21272.76	−0.30
11	2	20*	21253.06	21252.68	0.38
14	4	20*	21253.06	21252.49	0.57

TABLE I. (*Continued*).

v'	v''	Intensity	Frequency (cm^{-1}) Observed	Calculated	Observed-Calculated
24	10	0	21246.14	21248.28	−2.14
8	0	2	21242.20	21241.68	0.52
22	9	4	21236.63	21234.89	1.74
20	8	0	21213.19	21213.00	0.19
12	3	3*	21199.77	21202.49	−2.72
9	1	3*	21193.80	21194.07	−0.27
23	10	2	21170.96	21170.92	+0.04
21	9	3	21151.67	21152.43	−0.76
13	4	3	21151.67	21151.86	−0.19
10	2	30*	21146.27	21146.15	0.12
16	6	30	21146.27	21145.48	0.79
7	0	5*	21127.66	21129.77	−2.11
19	8	1	21125.86	21125.66	0.20
26	12	0	21102.85	21111.24	1.61
24	11	0	21102.85	21106.00	−3.15
11	3	20*	21097.59	21097.88	−0.29
17	7	1	21090.98	21091.06	−0.08
22	10	1	21090.98	21090.99	−0.01
8	1	2*	21083.78	21083.91	−0.13
20	9	1	21067.25	21067.50	−0.25
12	4	10*	21049.09	21049.20	−0.11
15	6	10	21049.09	21049.06	0.03
9	2	6*	21037.73	21037.78	−0.05
18	8	6	21037.73	21035.96	1.77
23	11	2	21028.73	21028.64	0.09
6	0	20*	21016.74	21016.18	0.56
21	10	1	21008.97	21008.53	0.44
13	5	1	21001.20	21000.10	1.10
16	7	1	20997.78	20996.82	0.96
10	3	2*	20991.55	20991.35	0.20
19	9	0	20978.90	20980.16	−1.26
7	1	10*	20972.20	20972.00	0.20
26	13	4	20965.01	20972.25	−7.24
24	12	0	20962.30	20965.37	−3.07
14	6	6	20948.85	20950.50	−1.65
22	11	6	20948.85	20948.71	0.14
17	8	1	20945.05	20943.96	1.09
8	2	2*	20928.35	20927.62	0.73
20	10	3	20924.37	20923.60	0.77
5	0	10*	20902.07	20900.96	1.11
25	13	2	20897.89	20901.09	−3.20
12	5	2	20897.89	20897.44	0.45
18	9	4	20891.32	20890.46	0.86
9	3	8*	20879.23	20882.98	−3.75
6	1	20*	20859.35	20858.41	0.94
13	6	1	20849.50	20849.87	−0.37
10	4	1	20835.14	20838.06	−2.92
19	10	1	20835.14	20836.26	−1.12
26	14	1	20826.11	20834.94	−8.83
24	13	1	20822.40	20826.38	−3.98
7	2	10*	20816.63	20815.71	0.92
22	12	1	20808.68	20808.08	0.60
17	9	1	20798.09	20798.46	−0.37
11	5	1	20793.05	20792.83	0.22
4	0	10*	20783.25	20784.19	−0.94
20	11	1	20779.87	20781.32	−1.45
8	3	10*	20773.17	20772.82	0.35
25	14	3	20760.57	20763.78	−3.21
23	13	1	20749.31	20749.02	0.29
18	10	1	20749.31	20746.56	2.75
5	1	8*	20743.74	20743.20	0.54
9	4	1	20728.87	20729.79	−0.92
21	12	1	20725.00	20725.62	−0.62

TABLE I. (*Continued*).

v'	v''	Intensity	Frequency (cm^{-1}) Observed	Frequency (cm^{-1}) Calculated	Observed-Calculated
13	7	0	20700.65	20701.21	−0.56
24	14	3	20686.07	20689.07	−3.00
10	5	3	20686.07	20686.30	−0.23
3	0	20*	20666.44	20665.89	0.55
20	12	3	20640.13	20640.69	−0.56
4	1	4*	20627.00	20626.42	0.58
25	15	2	20625.31	20628.15	−2.84
8	4	3*	20617.76	20618.13	−0.37
5	2	1*	20588.94	20586.90	2.04
21	13	0	20585.78	20586.63	−0.85
9	5	3*	20578.17	20577.93	0.24
24	15	2	20551.14	20553.44	−2.30
6	3	6	20548.83	20547.32	1.51
2	0	2*	20546.11	20546.14	−0.03
22	14	4	20531.59	20531.78	−0.19
7	4	2*	20507.92	20507.62	0.30
3	1	2*	20506.25	20508.12	−1.87
20	13	1	20502.04	20501.70	0.34
10	5	4	20484.82	20486.30	−1.48
23	15	1	20477.51	20476.08	1.43
4	2	15*	20470.18	20470.13	0.05
5	3	8*	20433.25	20432.11	1.14
1	0	8*	20426.39	20424.99	1.40
6	4	2*	20390.07	20391.03	−0.96
2	1	2*	20388.14	20388.37	−0.23
20	14	0	20364.25	20364.39	−0.14
25	17	1	20358.25	20362.03	−3.78
3	2	18*	20353.62	20351.83	1.79
23	16	2	20341.84	20342.16	−0.32
21	15	1	20314.03	20313.69	0.34
0	0	10*	20302.63	20302.49	0.14
24	17	1	20285.02	20287.32	−2.30
1	1	12*	20268.21	20267.22	0.99
2	2	4*	20232.10	20232.08	0.02
20	15	2	20227.99	20228.72	−0.73
7	6	3*	20204.59	20205.63	−1.04
3	3	5*	20198.66	20197.03	1.63
21	16	1	20180.63	20179.77	0.86

* Reported by Loomis.

Wood and identified by Loomis are indicated by an asterisk. The calculated frequencies are based on Eq. (1)

$$\nu = 20320.18 + 123.789(v' + \tfrac{1}{2}) - 0.6303(v' + \tfrac{1}{2})^2 - 0.009363(v' + \tfrac{1}{2})^3 - 159.23(v'' + \tfrac{1}{2}) + 0.726(v'' + \tfrac{1}{2})^2 + 0.0027(v'' + \tfrac{1}{2})^3 \qquad (1)$$

which has been developed by the method of least squares to fit most of the measured bands. The terms in v'' are equivalent to those previously given by Loomis[2] but those in v' required modification. As one can see from Fig. 1, wherein residuals are plotted against v', Eq. (1) is a good representation of the levels from $v' = 0$ to 24 but gives too high a value for levels 24 to 26, and is inadequate for extrapolation. For this reason the extrapolation to dissociation was made semi-graphically. The resultant estimated maximum value of T' is 23120 cm^{-1}, which when the atomic energy, 16966 cm^{-1}, is subtracted yields $D_0'' = 6154$ cm$^{-1} = 0.76$ volt as the energy of dissociation. Since the

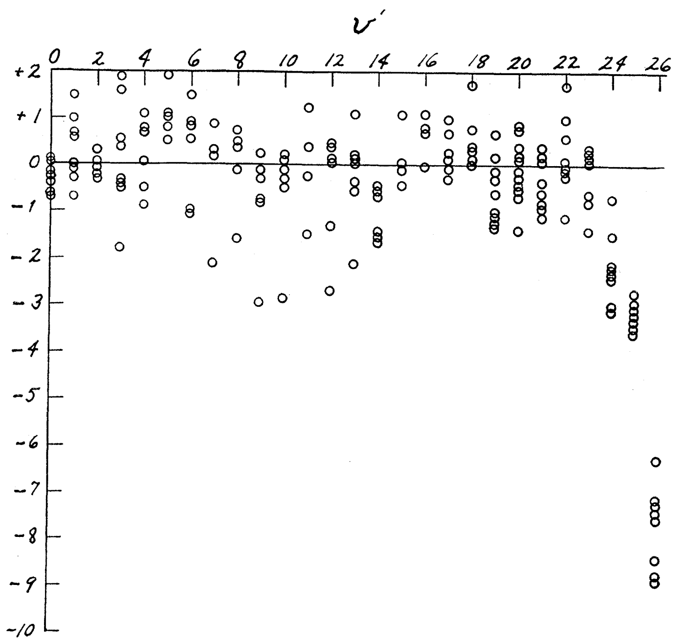

Fig. 1. Residuals of observed frequencies from Eq. (1).

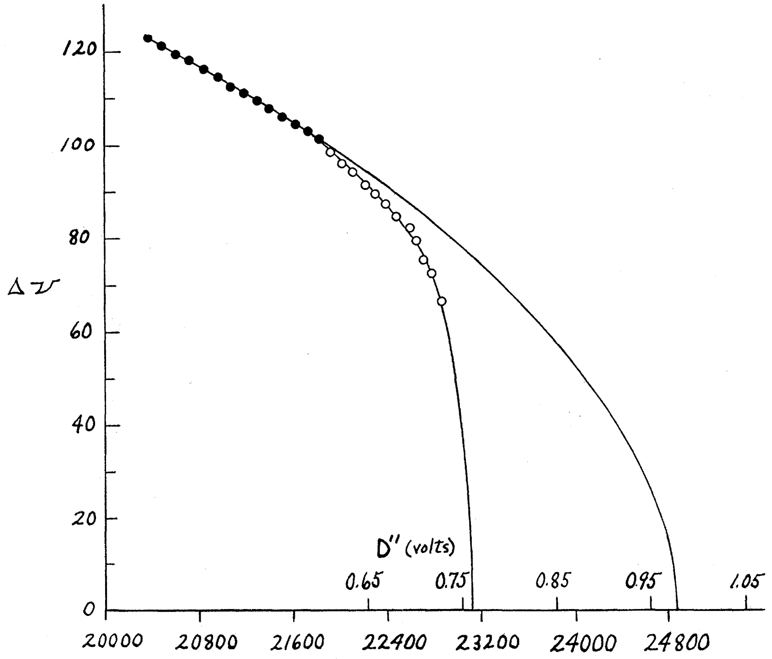

Fig. 2. $\Delta\nu$ vs T' extrapolated to dissociation. Full circles represent Wood's data, hollow circles new data. Upper curve is Loomis' extrapolation. Lower curve is new extrapolation. Upper scale of abscissae represents values of D_0'' which would be deduced from corresponding T' intercepts.

estimated dissociation lies only 0.02 volt above the highest identified level it cannot be too high by as much as this. It is harder to place a definite limit to the amount by which it might be too low but it can be seen from Fig. 2, in which the frequency interval, $\Delta\nu$, between adjacent levels is plotted against T', that it is probably safe to put the probable error of the extrapolation at ±0.02 volt.

Fig. 2 also shows the way in which a long extrapolation may be in error. The full circles represent the data of Wood, and the upper curve is Loomis' extrapolation based on them. The hollow circles represent the new data and the lower curve the new extrapolation.

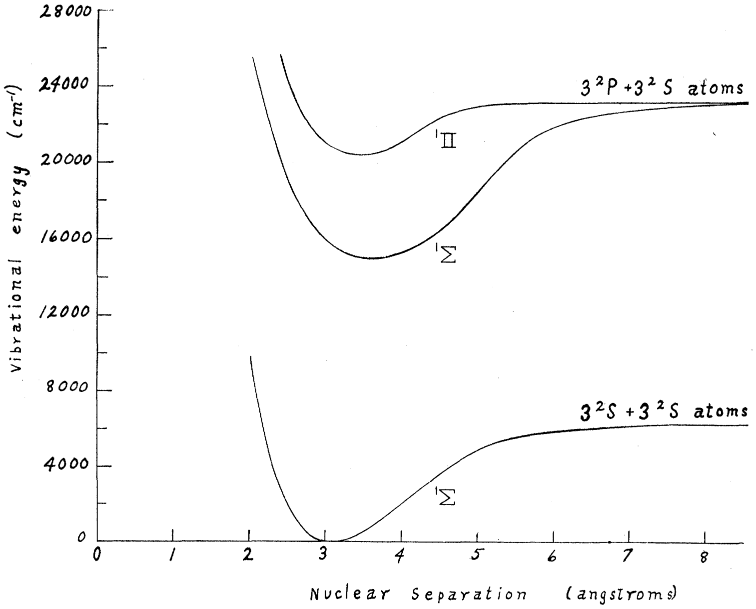

Fig. 3. Potential energy curves for the three accurately known levels of Na_2.

The heat of dissociation of sodium has been determined by several observers in different ways and with varying degrees of accuracy. Villars[4] made an extrapolation of vibrational levels like the above, but based on his own measurements of the absorption spectrum. He obtained a value of 1.16 volts but his series of levels was short and it was obvious that the extrapolation was less dependable than the previous one of Loomis. Polanyi and Schay[5] have estimated it as 0.80 volt, on the basis of experiments with low pressure flame and Rodebush and Walters[6] have published data on vapor pressure and vapor density from which it may be deduced that the heat of dissociation is about 0.8 volt. Ladenburg and Thiele[7a] by similar methods obtained the value

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[4] Villars, Proc. Nat. Acad. Sci. **14,** 508 (1928).

[5] Polanyi and Schay, Zeits. f. phys. Chem. **B1,** 36 (1928).

[6] Rodebush and Walters, J. Am. Chem. Soc. **52,** 2654 (1930).

[7a] Ladenburg and Thiele, Zeits. f. phys. Chem. **B7,** 176 (1930).

0.78 volt. Probably the best chemical determination is that of Lewis[7] who determined the ratio of atoms to molecules in a molecular beam in a Stern-Gerlach experiment and hence calculated $D_0''=0.73$ volt. This, as has been seen, is surely a little low. It is noteworthy that his values of the heats of dissociation of Li_2 and K_2 differ from ours by only 10 percent.

Fig. 3 shows potential energy curves for the three known states of Na_2. They are calculated on the basis of the data in the paper of Loomis and Nile[8] but the upper parts of the curves are adjusted to the new energies of dissociation. Fig. 4 shows the corresponding Franck-Condon diagram in the improved form described in our paper on lithium.

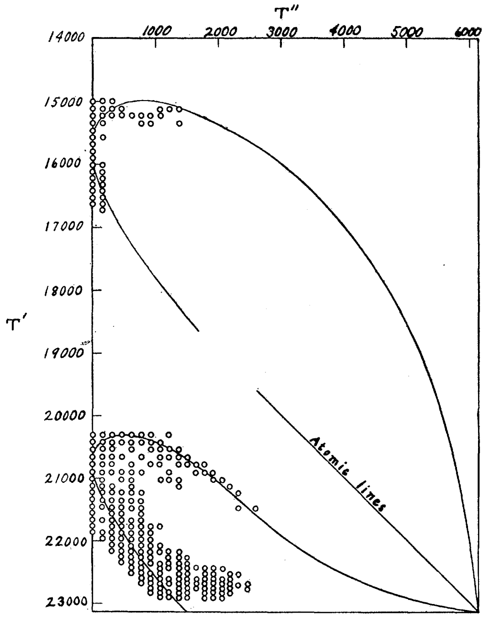

Fig. 4. Improved Franck-Condon diagram for the red and green systems.

In Table II are given values of the degree of association α of saturated sodium vapor as calculated by the equation of Gibson and Heitler from our constants and the vapor pressure equation of Rodebush.

TABLE II. *Values of the degree of association of saturated sodium vapor.*

T°C	Pm mm of Hg	K	α
200	0.000136	0.0420	0.9936
300	0.0134	1.24	0.9791
400	0.337	13.55	0.9537
500	3.67	80.49	0.9196
600	23.30	319.9	0.8800
700	100.3	966.2	0.8406
800	329.9	2374.	0.8017
883	758.2	4451.	0.7712

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[7] Lewis, Zeits. f. Physik **69,** 786 (1931).

[8] Loomis and Nile, Phys. Rev. **32,** 873 (1928).