THE ROTATIONAL STRUCTURE OF THE BLUE–GREEN BANDS OF Na2

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ABSTRACT

Because of the theoretically impossible structure of these bands as reported by previous observers, the writers have measured them, in absorption, in the third order spectrum of a seven inch plane grating mounted in a forty foot spectrograph. Each band is found, quite definitely, to consist of only one P, one Q and one R branch. This accords with Mulliken's theory that the electronic transition is $^1P - {}^1S$, and with the nature of the fluorescence series. Moreover the absorption series correlate properly with the fluorescence series. The combination relations have been applied to all measured bands and found to hold, rigorously, within the experimental error, except for the expected PQR defect, which is very small.

Constants of the band system.—The more important constants of this band system are: $B_0'' = 0.15431$, $I_0'' = 179.5 \times 10^{-40}$g. cm^2, $r_0'' = 3.08 \times 10^{-8}$ cm, $\alpha'' = 0.00082$, $B_0' = 0.12541$, $I_0' = 220.9 \times 10^{-40}$ g. cm^2, $r_0' = 3.41 \times 10^{-8}$ cm, $\alpha' = 0.00094$. These extremely large internuclear distances correspond to weak molecular binding, which is in accord with the low heat of dissociation previously reported. The locus of most intense vibrational transitions calculated from these constants and the previously reported vibrational constants, by the method of Franck and Condon, is found to be a good representation of the observed distribution. There is no evidence of alternating intensities.

T HE visible band absorption spectrum of Na2 consists of two distinct band systems, one in the red, the other in the blue-green. Each contains numerous overlapping bands and each band contains hundreds of lines, so that the spectrum is extraordinarily complicated. In complexity and line density it is about on a par with the spectrum of iodine.

The vibrational structure of the blue-green system has been analyzed and vibrational quantum numbers assigned by Loomis,[3,4] from a study of Wood's magnetic rotation spectrum.[5,6] The same assignment of vibrational quantum numbers has been reached by Fredrickson and Watson,[7] using their measurement of the frequencies of the heads in absorption, and is undoubtedly correct.

Rotational structure lines of what are now known to be the (1,1), (2,0), (3,0) and (5,1) bands were measured in absorption by Smith,[8] with a grating which gave a dispersion of 5A/mm and was able to resolve lines about 0.1A apart. He also arranged his lines into series, assigned quantum num-

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[3] Loomis, Phys. Rev. **29**, 607A (1927).

[4] Loomis, Phys. Rev. **31**, 323–332 (1928).

[5] Wood, Proc. Am. Acad. **42**, 235 (1906).

[6] Wood, Astrophys. J. **30**, 339 (1909).

[7] Fredrickson and Watson, Phys. Rev. **30**, 429–437 (1927).

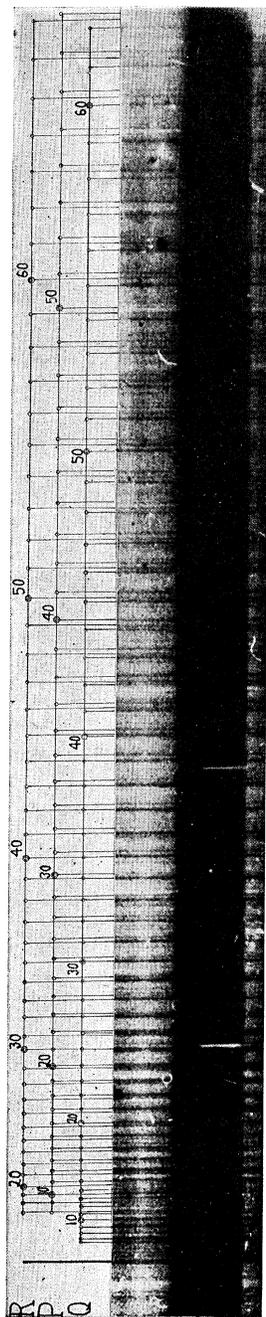[8] Smith, Proc. Roy. Soc. **A106**, 400–415 (1924).

Fig. 1. (0, 2) band. Numbers indicate values of j''.

bers to them, and calculated the moments of inertia of the molecule. He did not, however, check his assignments by the combination relations; and in fact when the PR combinations are tested on his data they fail completely. Moreover, the (1,1) band, as reported by him contains four branches, (R, Q, P, P') which, according to Mulliken's[9,10] system of interpretation of band spectra, is not a possible structure for molecules having an even number of electrons.

More recently the structure lines of the (1,0), (1,1), (0,1) and (0,2) bands have been measured by Fredrickson and Watson,[7] in the second order of a 21 ft. concave grating, giving a dispersion of 1.3/Amm. They arrange the lines of each band into four series which they call R, Q_R, Q_P and P, and which are quite different from those of Smith. They did apply the combination relations to check their arrangement into series and their assignment of quantum numbers, but their PR combinations show a systematic defect, and fluctuations of the order of magnitude of the line spacing. Moreover, the four branch structure which they report does not correspond to any of the types to be expected according to Mulliken's systematic theory of band spectra; certainly not to the $^1P - ^1S$ transition which is indicated by the character of the fluorescence series.[11]

The writers therefore felt that it was desirable to undertake new measurements of these bands, with higher resolution than previous observers have used, in the hope of finding series whose reality could be unambiguously established and of definitely determining whether or not these bands constitute an exception to Mulliken's system.

The spectrum was photographed in the third order of a 7 inch (17.8 cm) plane grating ruled with 14,000 lines per inch and combined in a Littrow mount with a 40-foot telescope lens as previously described by Wood.[12] This

[9] Mulliken, Phys. Rev. 28, 481 (1926).
[10] Mulliken, Phys. Rev. 28, 1202–1222 (1926).
[11] l.c. page 1216.
[12] Wood, Researches in Physical Optics, I, 27–29.

gave a dispersion of 0.4A/mm and resolved lines as close as 0.03A. The sodium was inserted in a steel tube about 80 cm long, to the ends of which glass windows were cemented. The tube was heated in a gas flame and the hydrogen thereby driven from the sodium was pumped off until a fairly steady pressure of a few mm was attained. The light from the crater of a carbon arc was then sent through the sodium vapor and into the slit of the spectroscope. The heating flame was carefully regulated to give just sufficient density of Na_2 to bring out the stronger lines fairly well, leaving the fainter lines inconspicuous. This condition was reached when the transmitted light was of a pale-green color and the corresponding absorption spectrum was relatively simple. If the temperature of the sodium was raised until the color of the transmitted light was deep blue, ahe absorption spectrum became very complicated and would probably have defied analysis. The absorption spectrum was photographed, with the iron arc lines for comparison, from 4890 to 5035A, as this region contains the origin of the system and the strong (0,1), (0.2), (1,0) and (1,1) bands which Fredrickson and Watson measured. It also contains a number of fainter bands.

A photograph of the (0,2) band, in which there is a minimum of overlapping lines, is reproduced in Fig. 1. It is evident that it consists of just three branches, as predicted by Mulliken's theory. The identification of the lines, as found from the analysis below, is indicated above them.

The other bands in the region studied are so complicated by overlapping lines that the series cannot be followed by inspection. They can, however, be followed in a table of computed line frequencies with estimated intensities, and it is quite evident that there are just three branches starting from near the head of each band. This will be apparent to the reader on inspection of Fig. 2. In this figure are plotted the differences between the frequency of every line in the *region* of the (0,1), (0,2), (1,0) and (1,1) bands, and the frequency of the adjacent Q branch line as calculated from Eq. (16) below. This method of plotting shows any series of lines which have roughly the same spacing as the Q branch, that is, any other branches of the same band, as a series of points lying along a smooth curve; whereas the lines of overlapping bands are represented by points scattered at random over the figure. The reality of the three series which appear in each band is even more evident when the intensities are noted, since in most cases the scattered points represent lines of lower intensity than those assigned to branches. It is then also apparent that the Q branch lines are, as predicted by Mulliken's theory,[13] definitely more intense than the R or P lines. In fact, in the (0,0) band, which is comparatively faint and overlapped by stronger bands, the Q branch is the only one which could be clearly demonstrated by this method.

It was next necessary to decide which series were P, which Q and which R branches and to determine which lines in each series had the same j''. Unfortunately the frequencies of the lines in Wood's fluorescence series are not quite accurately enough known to be used for this purpose; but

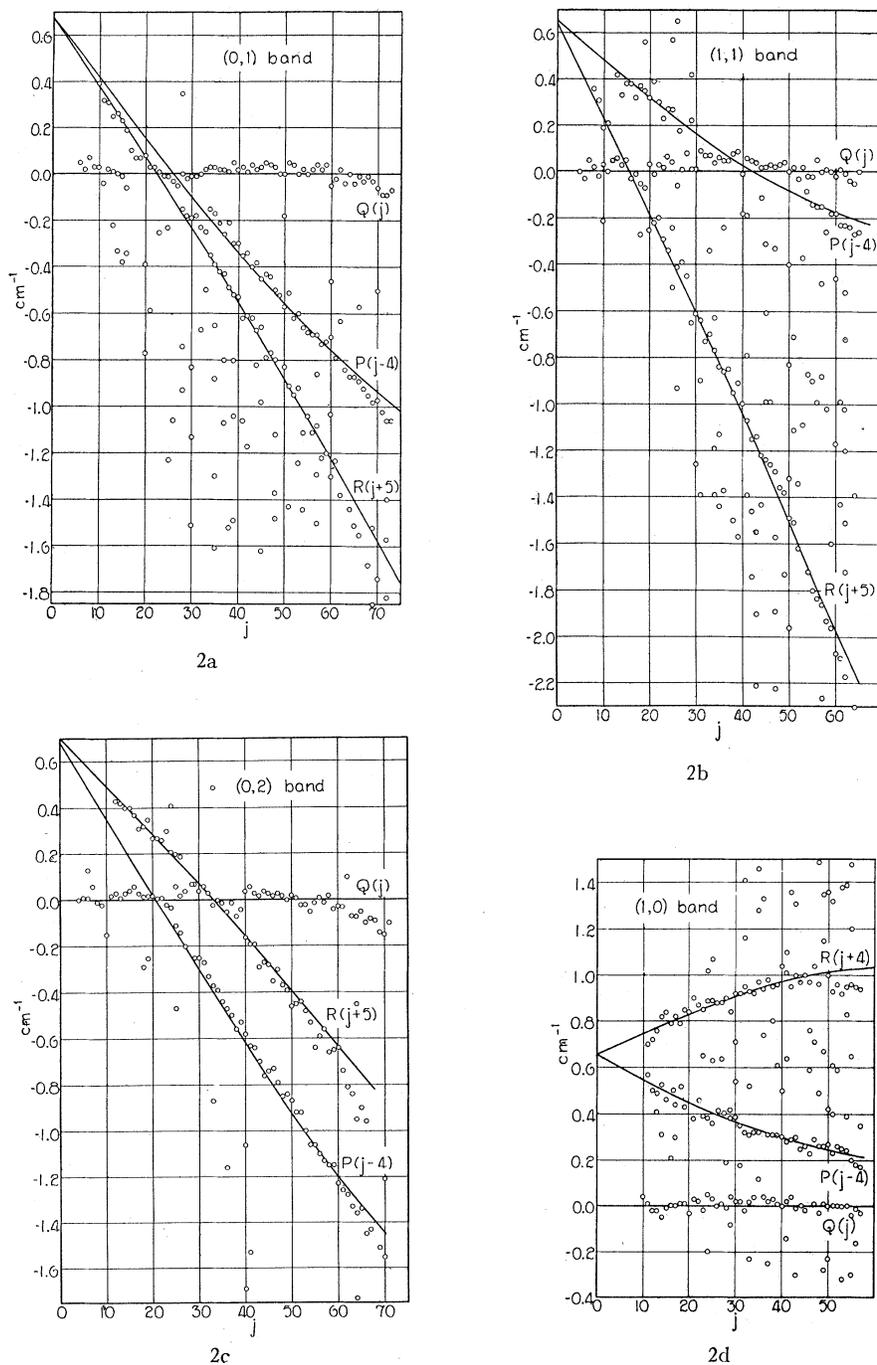[13] Mulliken, Phys. Rev. **29**, 391–412 (1927).

Fig. 2. $\nu - Q(j)$ for lines in the region of the four measured bands. $Q(j)$ from Eq. (16) and Table
I. The curves show the positions of the P, Q and R lines calculated from Eqs. (16) and (17).

the accuracy of the measured frequencies of the absorption lines is great enough to allow the determination to be made by the aid of the combination relations. This was done by a process of trial and error, using the fluorescence data to make tentative pairings of lines in the P and R branches. The final correct assignment of relative values of j'' to the P and R branch lines was attested by the agreement, within the limit of experimental error, of the values of

$$\Delta_2 F''(j) = R(j-1) - P(j+1) \quad (1)$$

for bands (0,1) and (1,1)

and $\Delta_2 F'(j) = R(j) - P(j)$ for bands (0,1) and (0,2) and for bands (1,0) and (1,1). In each case the next best assignment led to discrepancies between the $\Delta_2 F$'s which were definitely outside the experimental error over some part of the range. The exactness with which these PR combination relations hold may be seen in Fig. 3, wherein the residuals of the $\Delta_2 F$'s from functions obtained below, which represent them, are plotted against the j values, also obtained below. It is true that there are a few places in which there appear to be slight systematic differences between the $\Delta_2 F$'s, over a series of several values of j, but these occur where the lines of two branches of a band are unresolved; as may be seen by comparing with Fig. 2. In no case does the discrepancy become as large as the resolution of the grating.
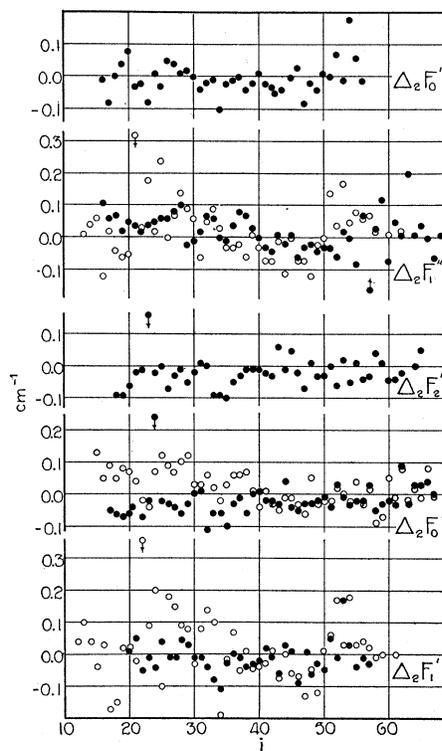

Fig. 3. $\Delta_2 F$, (observed)–(calculated by Eqs. (13) and (15)). Reading down, full circles represent data from bands (1, 0), (0, 1), (0, 2) (0, 2) and (1, 0); hollow circles represent data from bands (1, 1) (0, 1) and (1, 1).

It is not to be expected that the PQR combinations would hold exactly. This may be seen from Fig. 4, which illustrates the scheme of energy levels associated, according to Mulliken,[14] with a $^1P - {}^1S$ transition. Rotational doubling of the ^1P levels is to be expected. That is, there should be two terms, F_Q and F_{PR}, for each value of j, the F_Q terms taking part only in Q transitions, the F_{PR} terms only in P and R transitions. From an inspection of the diagram it can be seen that the "quantum defect"

$$[R(j) - Q(j+1)] - [Q(j) - P(j+1)]$$
$$= [F_{PR}'(j+1) - F_Q'(j+1)] + [F_{PR}'(j) - F_Q'(j)] \quad (2)$$

[14] Mulliken, Phys. Rev. **28,** 1205 (1926). The relative position of the PR and Q levels is here interchanged from that in Mulliken's figure, since this is how they happen to lie in Na_2, as is shown by the sign of the combination defect.

$$\sim 2\left[F_{PR}'(j+\tfrac{1}{2})-F_{Q}'(j+\tfrac{1}{2})\right]=2(B_{PR}'-B_{Q}')(j+\tfrac{1}{2})^2 \tag{3}$$

This quantity is plotted, for each of the four bands, in Fig. 5. The curve drawn through them is calculated according to (3) using $B_{PR}-B_Q=0.000013$, determined by least squares.

On account of the theoretically possible quantum defect, the above relations do not furnish an unquestionable check on the Q branches, though
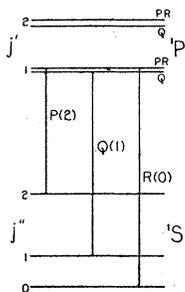
Fig. 4. Rotational energy levels and transitions associated with a $^1P-^1S$ electronic transition.
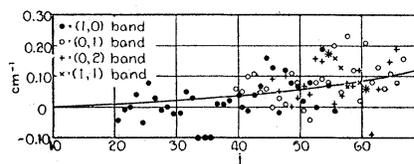
Fig. 5. PQR quantum defect.

the quantum defect is so very much less for this assignment of numbers than for any other, and so closely the same for all four bands, that there cannot be much real doubt. To make doubly sure however, the four band combinations have been applied to the Q branches. For this purpose data
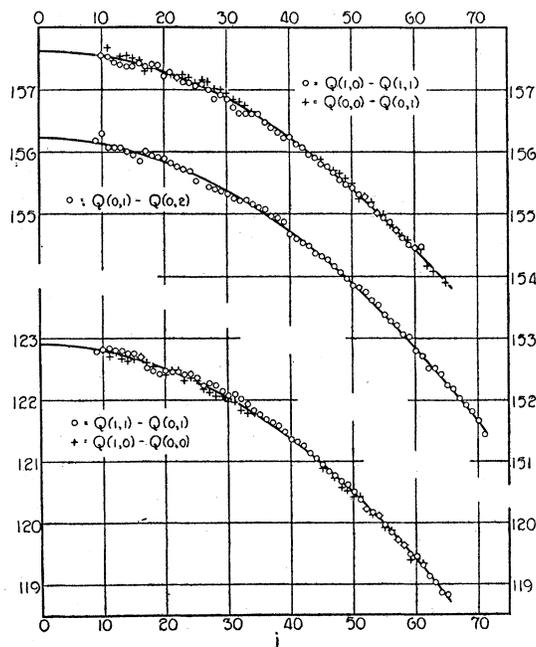
Fig. 6. Four-band Q branch combinations.

on the Q branch of the (0,0) band were also needed. Fig. 6 shows the result, which is quite conclusive. In the upper curve $Q(1,0) - Q(1,1)$ and $Q(0,0) - Q(0,1)$ are plotted and found to agree except where one of the four branches is overlapped by another. In the lowest curve, $Q(1,1) - Q(0,1)$ and $Q(1,0) - Q(0,0)$ are plotted and likewise agree.

When the above frequency differences had been obtained, the constants of the spectrum were computed by the following procedure. Absolute values of j were found by plotting the frequency differences $\Delta_2 F$, Eq. (1), against an assumed set of j's and extrapolating to zero. In each case, if the new mechanics formulation of the rotational term, $B[j(j+1) - \sigma^2]$ or its practical equivalent $Bj(j+1)$, is used, the values of j are found to be integral within the limits of error. They were therefore assumed in all subsequent calculations to be exactly integral and this assumption was later justified when more accurate least-squares computations were made after the $\Delta_2 F$'s had been corrected for the higher power terms in the energy. Approximate values of B' and B'' were found at the same time. Values of $B_0' - B_1'$, $B_0'' - B_1''$ and $B_1'' - B_2''$ and of $\Delta\nu_0$ were then found which were capable of representing the differences:

$$Q_{1,1}(j) - Q_{0,1}(j) = Q_{1,0}(j) - Q_{0,0}(j)$$
$$= \Delta\nu_0 - (B_0' - B_1')j(j+1) = 122.92 - 0.00094j(j+1)$$
$$Q_{1,0}(j) - Q_{1,1}(j) = Q_{0,0}(j) - Q_{0,1}(j)$$
$$= \Delta\nu_0 - (B_0'' - B_1'')j(j+1) = 157.64 - 0.00085j(j+1) \tag{5}$$
$$Q_{0,1}(j) - Q_{0,2}(j) = \Delta\nu_0 - (B_1'' - B_2'')j(j+1) = 156.23 - 0.00091j(j+1)$$

as follows:

$$B_0' - B_1' = 0.00094, \quad B_0'' - B_1'' = 0.00085, \quad B_1'' - B_2'' = 0.00091, \tag{6}$$

an approximate preliminary computation having first corrected for the effect of the nearly negligible higher power terms. The curves in Fig. 6 represent the frequency differences calculated from these constants.

A change of 0.00001 in any of the B differences above would just about make a sensible deviation of the curve from the plotted points, so the B differences may be assumed to be correct to about 0.00001. The difference between $B_0'' - B_1''$ and $B_1'' - B_2''$ is therefore real, and a linear formula is insufficient to represent the values of B''. The quadratic formula which does represent them is

$$B''(n'') = B_0'' - \alpha'' n'' - \alpha_2'' n''^2 = B'' - 0.00082n'' - 0.00003n''^2. \tag{7}$$

Since only one difference, $B_0' - B_1'$ is available in the upper level, the best that can be done is to assume that it is equal to α'.

$$B'(n') = B_0' - \alpha' n' = B_0' - 0.00094n' \tag{8}$$

The coefficients of the higher powers of j in the rotational terms could then be calculated. It was only necessary to carry the expansion as far as j^4, i.e.

$$F_n(j) = B_n[j(j+1) - \sigma^2] + D_n[j(j+1) - \sigma^2]^2 \tag{9}$$

In this expansion σ makes no practical difference. Here $D_0{}'$ and $D_0{}''$ can be calculated from Kratzer's[15] formula $D_0 = -4B_0{}^3/\omega_0{}^2$ and the other values of D can be found from $D_n = D + \beta''n$ after $(\beta'')'$ and $(\beta'')''$ have been computed from Pomeroy's[16] version of Kemble's[17] formula. For this purpose values of ω_0 and x were taken from Loomis' formula,[4]

$$\nu = 20301.7 + (124.13n' - 0.84n'^2) - (158.5n'' - 0.73n''^2 - 0.0027n''^3) \tag{12}$$

for the vibrational levels of the green system.

Corresponding to Eq. (9) for $F(j)$, the expression for the $\Delta_2 F(j)$ of Eq. (1) is

$$\Delta_2 F(j) = 4B(j+\tfrac{1}{2}) + 8D(j+\tfrac{1}{2})^3 \tag{13}$$

except for some negligible terms. The previously tabulated values of $\Delta_2 F$ can now be corrected by the addition of $-8D(j+\tfrac{1}{2})^3$ to give

$$\Delta_2 F^*(j) = 4B(j+\tfrac{1}{2}) \tag{14}$$

which should be strictly proportioned to $j+\tfrac{1}{2}$. From the tables of values of $\Delta_2 F^*$, B's were calculated according to Eq. (14) by least squares after it had first been ascertained by least squares that, with the values of j which had previously been assigned, there was actually no additional constant term in (14) larger than the limit of error of the determination; that is, that the j's were actually the integers which had been assumed. These values of B were than slightly adjusted, by no more than 1 in the last figure, to make them agree with Eqs. (6). The final values of B and D are as follows:

$$
\left.
\begin{aligned}
B_0{}' &= 0.12541 \\
B_1{}' &= 0.12447
\end{aligned}
\right\} \text{ for } P \text{ and } R
\qquad
\begin{aligned}
B_0{}'' &= 0.15431 \\
B_1{}'' &= 0.15346
\end{aligned}
$$

$$
\left.
\begin{aligned}
B_0{}' &= 0.12540 \\
B_1{}' &= 0.12446
\end{aligned}
\right\} \text{ for } Q \text{ branches}
\qquad
\begin{aligned}
B_2{}'' &= 0.15255 \\
D_0{}'' &= -0.5860 \times 10^{-6}
\end{aligned}
\tag{15}
$$

$$
\begin{aligned}
D_0{}' &= -4.076 \times 10^{-6} \\
D_1{}' &= -4.127 \times 10^{-6}
\end{aligned}
\qquad
\begin{aligned}
D_1{}'' &= -0.5907 \times 10^{-6} \\
D_2{}'' &= -0.5954 \times 10^{-6}
\end{aligned}
$$

Fig. 3 represents the residuals of the observed values of $\Delta_2 F$ from those calculated according to Eq. (13) with the constants in Eqs. (15). This figure shows at the same time the exactness with which the combination relations hold and the exactness with which the constants in (15) represent the observed values of $\Delta_2 F$.

The remaining unknown constant, the origin of the system, was found from the frequencies of each of a number of representative lines. The accepted average is ν_0 (0,0) = 20301.70.

[15] Kratzer, Zeits. f. Physik. **3**, 289 (1920).
[16] Pomeroy, Phys. Rev. **29**, 69 (1927).
[17] Kemble, J.O.S.A. **12**, 1 (1926).

The frequencies of the lines of the bands can now be calculated from the above constants according to the following equations;

$$Q(j) = \nu_0 + C_Q(j+\tfrac{1}{2})^2 + E(j+\tfrac{1}{2})^4 \tag{16}$$

$$R(j) \text{ or } P(j) = \nu_0 + B' \pm 2B'_{PR}(j+\tfrac{1}{2}) + C_{PR}(j+\tfrac{1}{2})^2 \pm 4D'(j+\tfrac{1}{2})^3 + E(j+\tfrac{1}{2})^4 \tag{17}$$

$$\text{where} \quad C_Q = B_Q' - B'', \quad C_{PR} = B_{PR}' - B'' \text{ and } E = D' - D''. \tag{18}$$

These are equivalent to the expressions deducible from Eq. (9) if a few negligible terms are omitted. The constants ν_0, C and E of the five bands measured are given in Table I.

TABLE I. *Values of the constants for the five bands measured.*

Band	ν_0	C_{PR}	C_Q	E
0, 0	20301.70	−0.02890	−0.02891	7.65×10^{-8}
0, 1	20144.06	−0.02805	−0.02806	8.12×10^{-8}
0, 2	19987.83	−0.02714	−0.02715	8.59×10^{-8}
1, 0	20424.64	−0.02984	−0.02985	7.02×10^{-8}
1, 1	20267.00	−0.02899	−0.02900	7.49×10^{-8}

Fig. 7 is a Fortrat diagram of the (0,2) band in which the observed frequencies are indicated by the circles and the calculated ones by the curves. On this scale the agreement appears to be perfect.
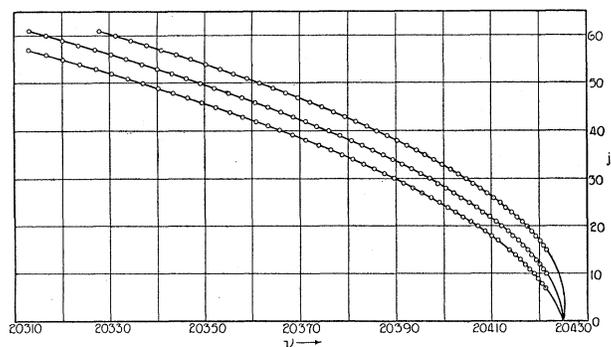

Fig. 7. Fortrat diagram of (0, 2) band.

In Fig. 2 the calculated differences between the lines of the several branches and the adjacent Q branch lines are represented by the curves. On this large scale it is apparent that there are slight but real systematic differences between the calculated and observed frequencies. However, they correspond to errors of only about 1 in the last figure of C and of 3 or 4 in the second figure of E, which are within the probable error of the determination of these constants from the $\Delta\nu$'s. It is not to be expected that constants determined from the $\Delta\nu$'s can be accurate enough to represent the ν's themselves adequately. The B's and D's could be adjusted within the probable error, to yield C's and E's which would accurately represent the ν's, but this procedure is not worth while, since it would not result in any gain in

accuracy in the B's. This is because each $C = B' - B''$ and there is no way to tell how to divide the adjustment between B' and B''.

The accurate values of B_0' and B_0'' in Eqs. (15) can now be used to calculate the moments of inertia and internuclear distances of the molecule according to the equations:

$$B_0 I_0 = h/8\pi^2 c = 27.70 \times 10^{-40} \tag{19}$$

$$I_0 = \tfrac{1}{2} m r_0^2 \tag{20}$$

Here m is the mass of a sodium atom, 3.80×10^{-23} grams. The resulting values of the molecular constants are:

$$I_0'' = 179.5 \times 10^{-40} \text{ g.cm}^2, \quad r_0'' = 3.08 \times 10^{-8} \text{ cm},$$
$$I_0' = 220.9 \times 10^{-40} \text{ g.cm}^2, \quad r_0' = 3.41 \times 10^{-8} \text{ cm}.$$

These are extremely large internuclear distances, indicative of a loosely bound molecule. They are therefore in qualitative accord with the small heats of dissociation, 1.0 volt in the lower and 0.6 volt in the upper state, already reported by Loomis.[4]

The present analysis of the structure of these bands is in harmony with the evidence of the fluorescence series. It is obvious that, if Fig. 4 is the correct energy level diagram, and the establishment of the PQR defect indicates that it is, then a fluorescence series should consist of doublets or singlets, according as the excited molecule happens to be in a PR or a Q state. All of Wood's data[5,6] on the fluorescence spectra of sodium excited by various line sources have been examined for the existence of series by a method like the one used by Loomis[18] to find iodine fluorescence series. That is, when, as is usually the case, the fluorescence lines fall naturally into groups separated by approximately ω'', these groups are assigned an "order" number p, starting with the group which contains the exciting line. (In some cases where there are many anti-Stokes lines it is more convenient to assign a "pseudo-order," p^*, starting with the lowest anti-Stokes group.) $\nu + T''(p)$ for each line is then plotted against p. In this arrangement singlet fluorescence series are represented by straight lines and doublet series by pairs of approximately parallel straight lines. The slope of the lines enables one to identify the bands to which the various members of the series belong. It was found that, while many of the fluorescence spectra are too complicated, resulting from simultaneous stimulation by too many lines, and often are too inaccurately measured, to permit unambiguous determination of series, there are many spectra in which definite singlet series exist, and a few in which there are definite doublet series, but none in which there is a triplet series. This is as it should be.

Moreover two of the doublet series, those excited by the 5086A line of Cd and the 5006A line of Pb, and a singlet series excited by Li 4972 have members which lie in the region where we have measured the absorption lines. These provide a further check on our work, since all members of a

[18] Loomis, Phys. Rev. 29, 112–134 (1927).

doublet series must correspond to P and R absorption lines having the same j' and n', and all members of a singlet series to Q lines having the same j' and n'. In Fig. 8 the fluorescence lines excited by Pb 5006A are represented
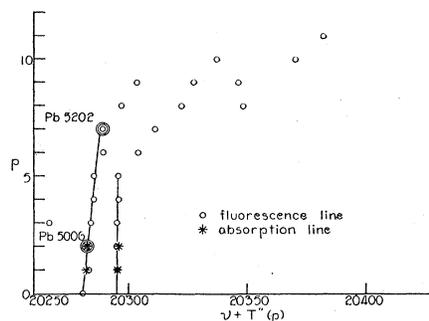

Fig. 8. Doublet fluorescence series excited by Pb 5006. P and R absorption lines with n'=0 and $j' = 21$.

by circles, using the coordinates described above, while the P and R absorption lines with $j' = 21$ from the (0,1) and (0,2) bands are represented by crosses. In Fig 9 the fluorescence lines excited by Cd 5086A are represented by circles and the P and R absorption lines with $j' = 36$ from the
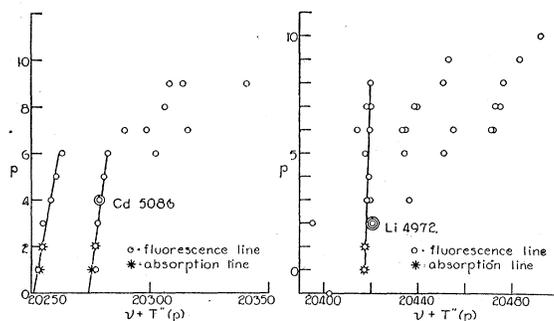

Fig. 9.   Fig. 10.

Fig. 9. Doublet fluorescence series excited by Cd 5086. P and R absorption lines with $n' = 0$ and $j' = 36$.

Fig. 10. Singlet fluorescence series excited by Li 4972. Q absorption lines with $n' = 1$ and $j' = 15$.

same two bands are represented by crosses. In Fig. 10 the fluorescence lines excited by Li 4972 are represented by circles and the Q absorption lines with $j' = 15$ from the (1,0) and (1,1) bands are indicated by crosses. It will be seen that the fluorescence and absorption frequencies agree within the apparent error of the measurements of the fluorescence spectra, and that the absorption frequencies lie more closely on the lines representing fluorescence series. Our absorption measurements are then very satisfactorily checked by the fluorescence series.

Two semi-empirical rules recently enunciated by Mecke and Birge and found to hold remarkably well in many varied spectra, furnish additional checks on the correctness of our analysis of these bands. The first rule is that B_0/ω_0 remains approximately constant during a transition.[19] Our values of the constants yield $B_0''/\omega_0'' = 0.00097$, $B_0'/\omega_0' = 0.00101$. The second rule[20] is that the quantity $R = 2xB_0/\alpha$ must be greater than 1, is usually between 1.2 and 2.2 and is roughly constant during a transition. Our constants yield $R'' = 1.73$, $R' = 1.81$.

The constants B_0'', B_0', α'' and α' obtained from the above analysis, together with ω_0'', ω_0', x'', x', D'' and D' from Loomis' analysis[4] of the vibrational structure, furnish sufficient data for a good determination of the locus of most intense vibrational transitions according to the method of Franck[21] and Condon.[22] Fig. 11 shows the potential energy in the lower
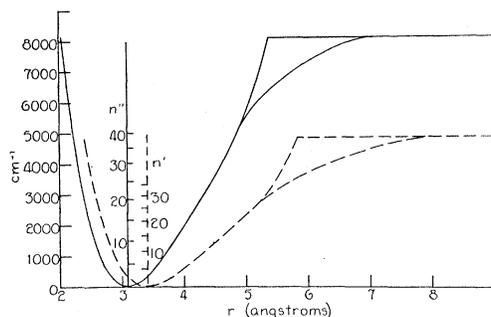

Fig. 11. Potential energy of Na₂ molecule as a function of internuclear distance. The lower state is represented by a continuous line, the upper state by a broken line.

state (continuous curve) and in the upper state (broken curve) as a function of internuclear distance r. The lower parts of these curves represent Taylor's series expansions about the equilibrium positions with coefficients calculated according to Condon's equations. The horizontal asymptotes represent the energies of dissociation. Smooth transitions between the two have been drawn in arbitrarily.

The curve in Fig. 12 is the (n', n'') locus of most probable vibrational transitions, obtained from Fig. 11 by Condon's procedure. The numbers in the circles represent the intensities of the magnetic rotation lines, plotted at the values of (n', n'') to which they were assigned by Loomis.[4] Although the curve deviates somewhat from the observed bands of high n'', as do most such curves, the agreement is on the whole excellent. The same curve represents equally well the absorption head measurements of Fredrickson and Watson.[7]

We have been to some pains to subject our analysis to all possible proofs because it is completely different from both those previously pub-

[19] National Research Council Report on "Molecular Spectra in Gases," page 233.

[20] Birge, private communication.

[21] Franck, Trans. Faraday Society (1925).

[22] Condon, Phys. Rev. 28, 1182–1201 (1926).

lished. Thus Smith's values of B are about 8 times and Fredrickson and Watson's from 2 to $2\frac{1}{2}$ times as great as ours; and the lines of Smith's series and of Fredrickson and Watson's series are spaced at more than double the intervals of ours. According to our analysis, lines of their "series" belong successively to a P branch, a Q branch, an unresolved chance pair of lines, etc. That is, their series are completely illusory, probably because of the lack of sufficient resolution. Since Fredrickson and Watson also considered the combination relations and the same fluorescence lines as evidence for the reality of their series it is necessary to give here a comparative summary of the evidence.

The following are evidence in favor of the reality of our series and the correctness of our analysis; (a) the type of band structure agrees with the existence of singlet and doublet fluorescence series and with Mulliken's
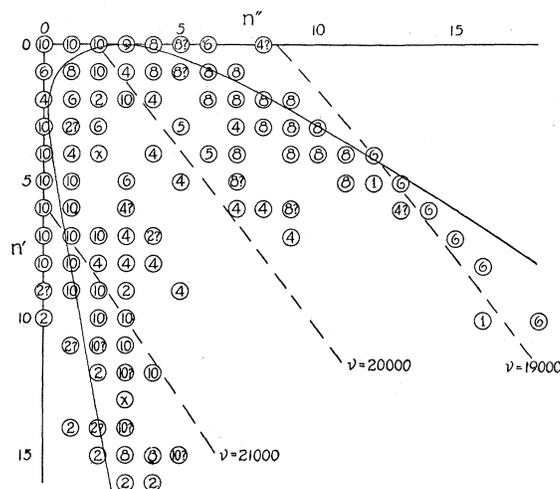

Fig. 12. Calculated locus of most probable vibrational transitions. Numbers in circles represent intensities of corresponding magnetic rotation lines.

theory; (b) three series are evident in each band in Fig. 2; (c) each series of fluorescence lines corresponds to absorption lines with a single j'; (d) and (e) the PR combination relations and the four band Q combination relations hold within the limits of error of measurement; (f) the PQR combinations show the same very small defect for each of the four bands, (g) the $\Delta_2 F$'s show a deviation from linearity for high values of j, and this deviation agrees with the theoretically calculated cubic term; (h) B_0/ω_0 and $R = 2 \times B_0/\alpha$ behave as predicted according to Birge and Mecke's semi-empirical relations; (i) when our constants are used to calculate the locus of (n', n'') for bands of maximum intensity, according to the Franck-Condon method, the curve obtained is a good representation of the observed distribution.

None of the above checks was applied by Smith to his series, and of those which can be applied, (a), (d) and (f) definitely disprove them. When applied to Fredrickson and Watson's series, (c) holds as well as it does for

ours; insufficient data are available for the application of (b), (e) and (g); the combinations (d) show systematic trends appreciably larger than the probable error, and large fluctuations; the combination defect in (f) is of the order of magnitude of $\Delta\nu$ itself; and (a), (h) and (i) definitely fail. In particular, the values of R calculated from Fredrickson and Watson's constants are $R''=0.32$ and $R'=0.18$ whereas, according to Birge's theory, R must always be greater than unity.

It should be mentioned that there is no evidence of any alternation of intensities in the absorption lines of these bands. Of course the intensities were estimated only visually, and any determination of intensities in absorption is notoriously rough, and there is here the complication of overlapping bands. Nevertheless the spectra show quite definitely greater intensities of the Q branch lines over the R and P lines, which should, on Mulliken's theory[13] be about half as intense. In many cases, near the tails of the bands, the R lines are perceptibly less intense, as they should be, than the adjacent P lines, but still show no trace of alternating intensities. It is probably safe to say that there is no alternation of intensities with a ratio between adjacent lines of over 3/2 or even 4/3.

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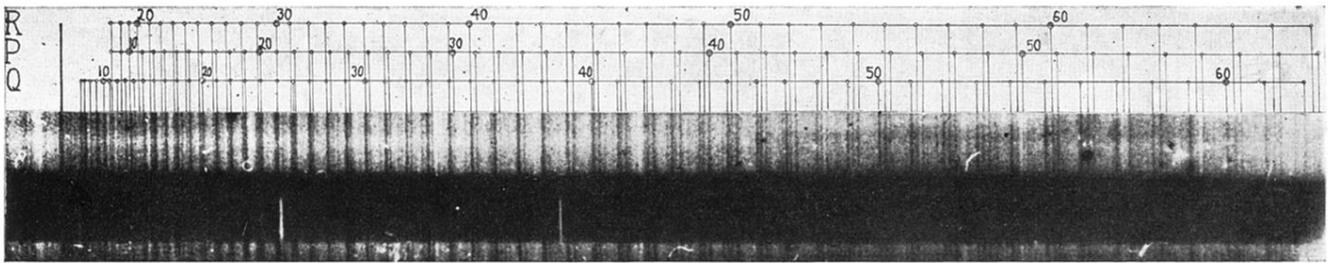   TUXEDO PARK, N. Y.
            April, 1928.

Fig. 1. (0, 2) band. Numbers indicate values of j''.