EXPERIMENTAL DETERMINATION OF RELATIVE TRANSITION PROBABILITIES IN THE SODIUM ATOM

By George R. Harrison[1]

Abstract

Determination of the relative transition probabilities for lines 2 to 16 in the principal series of sodium.—*Direct measurement of line absorption intensities* was made by a precise method of photographic photometry previously described. On each plate 11 spectra were photographed, 5 absorption spectra of light from an aluminum underwater spark which had passed through 10 cm of vapor, and 6 calibrating spectra of a constant cadmium spark. Corrections were applied for densitometer slit width, plate characteristics, band absorption, and sensitometer slit width and dispersion curve. The doublets were unresolvable at the vapor pressures used and were treated as single lines. Line shapes were measured at 18 different vapor densities, covering a four-fold variation, and from these were determined the constants C_1 and C_2 in Slater's formula for transition probabilities as given by his theory of virtual oscillators, $Nxh\lambda_0 B_{ij} = c\pi\log_e 10 \times \sqrt{C_1/C_2}$, and the relative transition probabilities B_{ij} for the various lines 2 to 16. No decrease in relative probability of the higher numbers with increasing vapor pressure was found, the curves for $\log_{10} NB_{ij}$ as a function of term number for different pressures being practically parallel. From the smoothed curves average *relative values of B_{ij}* were obtained with a variation of 2 to 4 percent, and from these the corresponding *relative values of A_{ij}* were calculated from Einstein's relation $c^3A_{ij} = 8\pi h\nu_0^3 B_{ij}$. Hoyt's preliminary theoretical calculation of the ratio of the first two terms was found to agree closely with these results.

Introduction

The formulation of Einstein's probability laws and of Bohr's correspondence principle has made the experimental determination of the intensities of spectrum lines, and of the magnitude of absorption coefficients, of increased importance, and examination of the literature reveals the very small amount of work that has been done in these fields.

A number of theoretical papers have recently appeared applying these generalizations to the prediction of the amounts of absorption to be expected in the various lines of certain series and in certain regions of continuous absorption. Kramers[2] has derived the λ^3 law for continuous absorption at the limit of series in the x-ray region, while Milne[3] obtains a λ^2 law for the similar absorption at the limits of series in the optical

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[1] National Research Fellow.

[2] Kramers, Phil. Mag. **46**, 836 (1923)

[3] Milne, Phil. Mag. **47**, 209 (1924)

region. Thomas,[4] assuming Fues'[5] values for the potential gradient in the sodium atom, has calculated the absolute value of the probability A_{ij} for the D-lines of sodium, and the relative probabilities for the second and third members of its principal series. Since the question of the proper method of averaging to be used in applying the correspondence principle to the determination of intensities has not yet been settled, Thomas gives ten sets of values for the relative probabilities, using different possible means. Hoyt[6] has recently calculated the relative values of A_{ij} for the first three lines in sodium and rubidium, breaking up the orbit of the electron into short lengths and making certain approximations for the regions between. All theoretical workers in this field emphasize the great number of uncertainties introduced by the assumptions necessary, and regret the absence of more experimental data for checking results.

Practically the only set of experiments which can be used for comparison are those made by Bevan,[7] in which he measured the relative amounts of dispersion obtained near the first three lines of sodium, the first four of potassium, and the first six of rubidium. Ladenburg[8,9] has shown how Bevan's data can be interpreted in the light of the quantum theory and can be made to give the relative A_{ij} values of the lines. Bevan found that his measurements for the last lines given in each case began to be uncertain, and was unable to get data for higher members. He found also that his constants varied with vapor density, the higher members appearing less intense at high vapor pressures.

A great deal of work has been done on the relative intensities of the two D-lines, and these are generally taken as having the ratio 2:1, the short-wave member being the more intense. Füchtbauer[10] and his collaborators have measured the relative intensities of the first members of the principal series of Cs and Rb in absorption, besides studying the effect of pressure on the shapes of the first lines of Na and K, using a direct method. So far as is known, however, no other exact comparisons of successive intensities of lines in a series have been made beyond those listed. It appears then that the direct measurement of the variation in

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[4] Thomas, Zeits. f. Phys. **24**, 169 (1924)

[5] Fues, Zeits. f. Phys. **11**, 364 (1922); **12**, 1 (1923)

[6] Hoyt, Phys. Rev. **25**, 174 (1925); also manuscript of paper in preparation.

[7] Bevan, Proc. Roy. Soc. **85**, 58 (1911); **84**, 209 (1910)

[8] Ladenburg, Zeits. f. Phys. **4**, 451 (1921)

[9] Ladenburg and Reiche, Die Naturwissenschaften, Bohrheft, **27**, 584 (1923)

[10] Füchtbauer, Phys. Zeits. **21**, 322 (1920);
Füchtbauer and Schell, Phys. Zeits. **14**, 1164 (1913);
Füchtbauer and Hoffmann, Ann. der Phys. **43**, 96 (1914)

absorption across narrow spectrum lines, and the comparison of successive lines in a series, while a very important problem, has received comparatively little attention.

EXPERIMENTAL ARRANGEMENTS

The amount and variation of the continuous absorption at the limit of the principal series in sodium vapor has been measured by the writer,[11] using a method of photographic photometry which admits of considerable precision. A similar method was used in the present work, in which the relative intensities of the first fifteen absorption lines after the D-lines, were measured. For the details of the photometric method the reader is referred to the previous paper. The absorption furnace, sensitometer, and densitometers were the same, the chief differences being in the light source and in the method of measuring and reducing the plates.

In measuring the continuous absorption it was necessary to have light of constant intensity, more or less uniform over a wide band of wave-lengths. Occasional emission lines in the source made little difference, but it was absolutely necessary that there be no spectral energy variation in the source between the exposure for the absorbed spectrum and that for the unabsorbed spectrum. In the present work, no emission line could be allowed in the neighborhood of an absorption line being measured, but variations of spectral energy distribution were of small consequence, producing second order errors. This was due to the fact that each line covered such a narrow wave-length range, and the density variation in that region was turned directly into intensity variation by means of the plate calibration.

Eleven spectra, all of the same time of exposure, were photographed on each plate. Six of these were of the constant intensity cadmium spark, taken through wire screens of known transmission, as described in the previous paper. The other five were absorption spectra of the sodium vapor, using as a back-ground either the cadmium spark used for calibrating or an aluminium under-water spark fed by a Tesla coil. Although this spark could not be made as steady as the spark in air, its variations could be neglected when measuring line absorption coefficients, if kept to a minimum, since the center of the line was being compared with its edge. The presence of an emission line in the source anywhere near an absorption line could not be allowed, however, since then even a narrow region could not be expected to remain constant in distribution. All results given in this paper were taken with at least two different back-

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[11] Harrison, Phys. Rev. **24**, 466 (1924)

grounds, so that errors from this source were eliminated. The calibration of the plate was in every case made with the constant-intensity cadmium spark.

A narrow slit was used on the Fuess quartz spectrograph of the sensitometer so as to get as much resolving power as possible. The dispersion used varied between 19A per mm at 3300A and 6.5A per mm at 2500A. It will be evident from what follows that the most important corrections, after those having to do with the calibration of the photographic plate, were those made necessary by the finite resolving powers of the sensitometer and the densitometer.

The instruments used for measuring the plates in this and the preceding work have been described in detail in a paper recently published.[12] Since their precision was known to be closer than to within one-fourth of one per cent where direct measurements of density were made, the chief errors which had to be taken account of were those due to inaccuracy in plate setting, and on the steep edge of an absorption line this became of great importance. Accordingly the running densitometer was so arranged that the plate was driven across the slit by an accurate screw provided with a wheel and ratchet, such that one click corresponded to an advance of .01 mm. The number of readings taken across each line varied from thirty for the more intense to ten for the weaker lines.

The high sensitivity and accuracy of the densitometer was attained by using a contact slit, the plate being placed emulsion side down over it. Where high densitometer resolving power was desired, this necessitated using a very fine slit and having it arranged so that it could be raised or lowered slightly to bring it almost into contact with the emulsion. Unless all lines were measured with the slit the same distance from the emulsion, errors would result due to the variation in resolving power, and since practically all plates are concave on the emulsion side, great care had to be taken in this regard. The plates were tightly clamped to a carriage, and the slit was always adjusted so that it practically touched the emulsion, its surface being slightly convex to avoid scratching. The equivalent width of the slit at the emulsion was measured by moving an artificial line across it, made by scratching a fine groove in a dense portion of the plate. This equivalent width was always slightly greater than the actual slit width, due to curvature of the spectrum lines, to lack of accurate parallelism between the slit and lines, and to the divergence of the light beam while passing through the emulsion. The spectrograph of the sensitometer was adjusted so that the lines would be as straight as possible,

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[12] Harrison, J. Opt. Soc. Amer. and R.S.I. **10**, 157 (1925)

and care was taken that its slit was evenly illuminated, to avoid any density variations along the lines.

On account of the low dispersion used and because at the vapor densities necessary for absorption of the higher members the two lines of each doublet coalesced, each absorption curve was treated as being due to a single line. With the resolving power here used no dissymmetry could be detected in even the strongest lines, although it probably would have been observable had not the band absorption masked it.

Since in order to get the results given below for eighteen different vapor densities at temperatures between 450°C and 600°C over 5000 density measurements had to be made on the various plates, it was necessary to simplify the method of reduction to keep the number of calculations within reasonable limits. This was done by slightly changing the method of plotting the characteristic curves of the plates.

The straight-line portion of a "H and D," or "characteristic" curve for a photographic plate at any wave-length is generally represented by an equation of the form

$$d=\gamma \log_{10} It^{p} - \text{const.}$$

where d is photographic density, γ the contrast, I the light intensity striking the plate, t the time of exposure, and p Schwarzschild's constant, while the additive constant depends on the inertia of the plate at that wave-length. This equation may be written

$$d=\gamma \log_{10} I+p\gamma \log_{10} t-\text{const.}$$

But d is defined as the common logarithm of the opacity O, which in turn is the ratio of the light incident on the plate in the densitometer to that passing through it. Calling these L and L' respectively, we have

$$d=\log_{10} O=\log_{10}(L/L')=\log_{10} L-\log_{10} L' \ .$$

Substituting this value of d in the second equation above, we have

$$\log_{10} L-\log_{10} L'=\gamma \log I+p\gamma \log_{10} t-\text{const} \ .$$

In the present work densities were compared only for points having the same time of exposure and the same wave-length, so we may include the t term with the additive constant. Also, in the densitometer the light incident on the plate was always kept constant while points were measured whose densities were to be compared, so L remained the same. Grouping the constant terms together, we have

$$-\log_{10} L'=\gamma \log_{10} I+\text{const} \ .'$$

Hence, since galvanometer deflections are directly proportional to L', if we plot these on logarithmic paper against I, we obtain an inverted characteristic curve, having the negative slope of the original H and D curve, and being quite as convenient for reduction purposes. This method reduces the number of operations required for changing galvanometer deflections to sensitometer light intensities, since one need only plot the deflections for the proper wave-length of the calibration spectra against the known intensities of the light producing them as determined by the absorption screens, and then read off from the resulting curve the intensities corresponding to the deflections obtained for the absorption curve. The process of keeping L constant not only means keeping the lamp voltage the same in the densitometer, but also being sure that the plate fog is fairly uniform. Since the absorption lines being measured cover such a narrow wave-length band, it is only necessary to make one calibration curve for each line on each plate. It should be noted that we are not restricted merely to the straight-line portion of the curve, the reversed heel and shoulder portions being usable, though not with such accuracy or convenience because of their smaller slopes.

Before changing densities into intensities the galvanometer deflections were corrected for the finite width of the densitometer slit. There are several ways of making this correction, one of the most convenient having been derived by Slater[13] for the case of a spectrograph slit, but being also applicable in the present case. This method was not available for the correction of the densitometer measurements used in this paper, however, although it was used for the sensitometer slit corrections. The method used, while somewhat more cumbersome, gave results of sufficient accuracy. Its derivation follows.

If we have a certain opacity gradient in that region of the absorption line subtended by the slit, the resulting deflection of the galvanometer will be that due to the average opacity of the region. This opacity will allow a light intensity L_1' to pass through the plate, the corresponding deflection being p. The region of width σ subtended by the slit may be considered as made up of m equal parts of width Δx, each illuminated by an intensity l_1, l_2, ... etc. due to the average opacity across its breadth. Then

$$L_1'\sigma = \Delta x(l_1 + l_2 + l_3 + \;.\;\;.\;\;.\;\;.\; + l_m)\;.$$

Now, if the plate be moved across the slit a distance Δx, one of the narrow portions will be dropped out and a new one added, causing a new average opacity over the whole slit, and a new intensity L_2' to fall on the thermopile of the densitometer. Hence

$$L_2'\sigma = \Delta x(l_2 + l_3 + \;.\;\;.\;\;.\;\;.\; + l_m + l_{m+1})\;.$$

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[13] Slater, following article in this issue.

Then $$\sigma(L_2'-L_1')=\Delta x(l_{m+1}-l_1)\ .$$

But $\sigma=m\Delta x$, so $m(L_2'-L_1')=l_{m+1}-l_1\ .$

Now $L'=p\times$const., and l will also be proportional to p with the same constant if allowed to shine through the whole width of the slit. Hence, by adding m times the difference between the nth and $(n+1)$th actual readings to the nth true reading, we obtain the $(n+m)$th true reading, where by true readings are meant the readings for the average opacity over the narrow region Δx. In order to begin somewhere with a true reading it was only necessary to start on a region of uniform opacity, such as the edge of an absorption line, and then proceed according to the above rule. The chief fault of this method lies in the fact that errors are cumulative, and when the point of maximum absorption has been passed they become quite serious. For this reason each line was calculated from one side to a point past the maximum absorption, and then the rule was reversed and the second half of the line calculated backwards, the two sets of values being averaged where they overlapped.

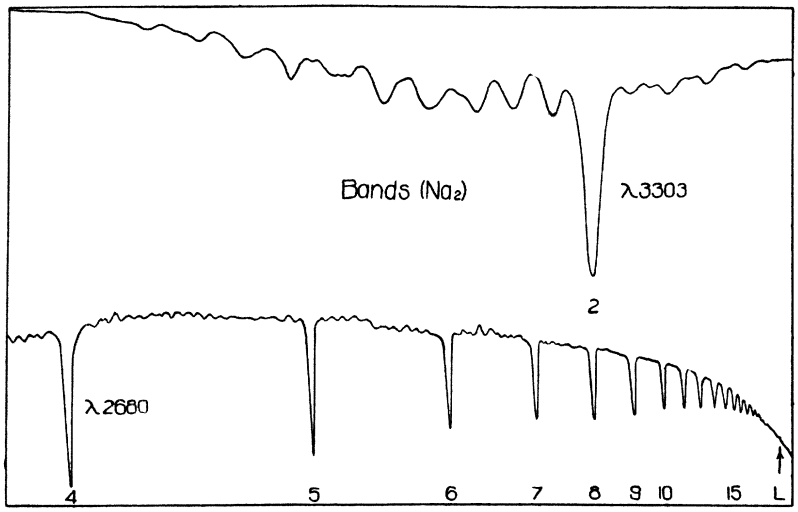

Fig. 1. Densitometer tracings of portions of a sodium vapor absorption spectrum, showing the type of density variations measured and the band absorption surrounding the lines.

In Fig. 1 are shown typical densitometer tracings of two portions of a sodium absorption spectrum at moderate vapor density. This shows the magnitude of the band absorption, especially around the lower members. At the very highest densities used the bands completely obliterated any evidence of either the second or the third lines. The D-lines are completely overwhelmed by their surrounding bands at the vapor pressure shown, and for this and other reasons they were not measured in the present work. The bands have been recently[14] shown to be due to Na_2, and some work of the writer[15] has indicated that they could be decreased in intensity by using unsaturated vapor at high temperatures. This has recently been confirmed for potassium vapor,[16] which has analogous bands, as have all the other alkali metals. Accordingly, it is desirable that the present work be repeated at high temperatures with unsaturated vapor, and it is intended to do this, although the experimental difficulties of the photometry will be greater, while the theoretical interpretation will not be so simple due to the number of excited atoms present.

The difficulties due to the bands were overcome, although, as the tracings show, the assumption of uniform opacity at the edges of the lines was not justified. Inspection of tracings of each line indicated the corrections which had to be made, however. The tracings were taken with continuous motion of the plate at the rate of one inch an hour, while all measurements were made with the plate at rest, to avoid errors due to galvanometer lag. In the most intense lines differences in deflection of as much as 50 cm were obtained between the edge and center of the absorbed region.

A number of preliminary plates had to be taken in order to determine the best time of exposure and set of light intensities to be used for each set of vapor densities. This was of great importance for accuracy, since the calibration points not only had to lie in the same density regions as the points on the absorption curve, but it was desirable to use as far as possible the straight-line portion of each characteristic curve to increase the precision of measurement. Due to the wide variation in density between the center of the most strongly absorbed line and the edges of the line in the region of greatest density of background, this became a matter for nice adjustment, especially since several vapor densities were taken on each plate, and on account of band absorption and scattering the background was reduced to as little as one-eighth of its original intensity for the higher vapor densities. Variations of 100-fold in the light intensity were available on each calibration curve.

Fig. 2 shows graphically the various corrections applied in a given line to change galvanometer deflections into transmissions. After the deflections were corrected for slit width, they were changed to light intensities by means of the proper characteristic curve for their central wave-length.

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[14] Smith, Proc. Roy. Soc. **A106**, 400 (1924)

[15] Harrison, Proc. Nat. Acad. Soc. **8**, 260 (1922)

[16] Sur and Ghosh, Phil. Mag. **49**, 60 (1925)

Using the average intensity of the two edges of the line as unity, and assuming that this intensity would have been uniform across the line if no absorption had taken place, the transmission curve across the line was then plotted. A number of these transmission curves for the same line at different vapor densities were then compared, and no regular dissymmetries were found. The two sides of each line were then averaged together, and the resulting transmission curve was corrected for the sensitometer slit width by the method of Slatter.[13] Finally, the ratios (I/I_0) obtained were tabulated with their corresponding $(\lambda-\lambda_0)$ values, as shown in Table I.

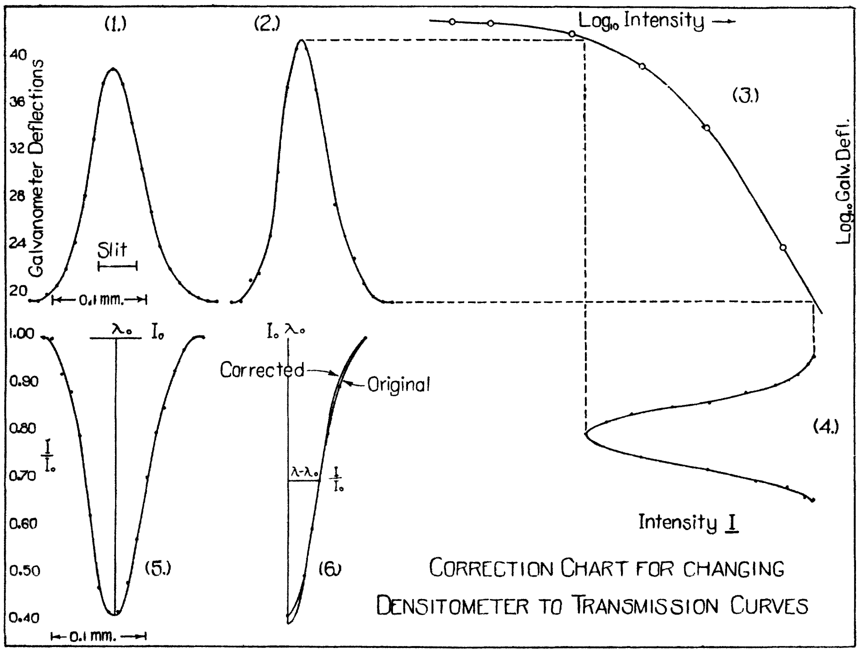

Fig. 2. Chart showing the corrections which were applied to galvanometer deflections of the densitometer to obtain the true transmission curve of an absorption line. The original deflections, plotted in (1) against distances along the plate, were corrected for densitometer slit width in (2). These deflections were then transformed into light intensities striking the plate at the wave-length considered, by means of the calibration curve shown in (3). The resulting light intensities, in (4), were changed into percentage transmission in (5), by comparison with the value of I at the edge of the line, which was taken as I_0. Finally, in (6), the two sides of the line were averaged and corrected for sensitometer slit width.

RESULTS

By the above method, and from data similar to that given in the first and third columns of Table I, the depths, breadths, and areas of the second to sixteenth lines of the sodium principal series were determined at eighteen vapor densities, some of the weaker lines being omitted at the lower densities, and some of the stronger ones at the higher. One hundred and eighty tables similar to the above were thus made. Detailed tabulation of the depth, breadth, and area values would have little worth, however, since theory indicates that the exponential law cannot be expected to hold for such narrow regions of absorption by atoms. Instead the data were used to calculate the relative transition probabilities for the different stationary states in the sodium atom, and also the relative numbers of atoms absorbing in each case.

TABLE I

Plate 26a. Spectrum 9. Line 3 (2853 A)

$(\lambda-\lambda_0)$	$(\lambda-\lambda_0)^2$	I/I_0	Values of $-1/\log(I/I_0)$ $R=1.00$	 $R=1.047$	 $R=1.07$
0	0	.38	2.38	2.27	2.22
2	4	.40	2.51	2.39	2.33
4	16	.49	3.22	3.03	2.94
6	36	.57	4.10	3.79	3.65
8	64	.66	5.55	5.00	4.76
10	100	.72	7.00	6.13	5.78
12	144	.80	10.3	8.54	7.87
14	196	.84	13.1	10.4	9.43
16	256	.89	19.6	14.1	12.3
18	324	.93	32.3	19.6	16.4

$c_1=25.1$ $R=1.07$ $C_2=2.2$

The method used to obtain these results has been outlined by Slater.[13] He obtains the formula

$$B_{ij}=\frac{3.31\cdot 10^{37}}{Nx\lambda_0}\cdot\sqrt{\frac{C_1}{C_2}}$$

where B_{ij} is the probability of a transition from state i to state j caused by the absorption of radiation, e is the base of natural logarithms, c the velocity of light, N the number of absorbing atoms, x the length of absorbing path, h Planck's constant, and λ_0 the central wave-length of the absorption line, while C_1 and C_2 are constants for a given line obtained from the formula

$$(\lambda-\lambda_0)^2=C_1[-1/\log_{10}(I/I_0)-C_2]$$

which gives the shape of the line. Hence, if $(\lambda-\lambda_0)^2$ is plotted against $-1/\log_{10}(I/I_0)$ a straight line should result. Values for a typical line are plotted in Fig. 3, the data used being given in Table I. When the first curve was plotted it was found to be convex upwards. Dr. Slater noted, however, that if the value of I_0 was multiplied by a small factor R the curve became a straight line; this result indicated that the failure to obey the formula was due to the band absorption which masked the true edge of the line, this being much wider at its top than at first supposed. In every one of the many cases in which this method was applied the factor had a value lying between 1.03 and 1.20, indicating that the result was not accidental. In most cases the points fitted a straight line better than in that illustrated, and in a few not quite so well, but for every absorption line the value of the factor R which made the points most closely approximate a straight line was found by trial and error. The value of C_2 was obtained from the intercept of this line, and the constant C_1 from its slope c_1 by multiplying by the square of the dispersion of the spectrograph for that wave-length in angstrom units per .02 mm, c_1 being in .02 mm units. After C_1 and C_2 had been found it was possible at any time to get the depth, half-breadth, and area of the line from them by Slater's formula.

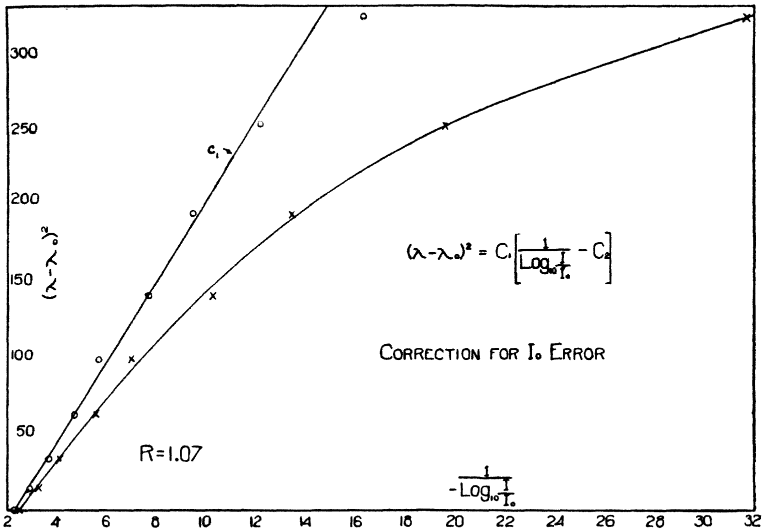

Fig. 3. The curve marked with crosses gives the data involving line shapes as originally measured; the curve marked with circles gives the corrected data as plotted after the best value of R had been found by trial and error to give the nearest approach to a straight line.

After the constants had been determined for all of the lines which could be measured at a given vapor density, they were independently plotted against the term number of the line to which they belonged. An example of this is shown in Fig. 4. The values of c_1 were plotted instead of those of C_1 because its curve was of simpler form. The general nature of the smooth curve connecting the points being evident, each constant was corrected by adjusting its value to fall on this curve. Due to the numerous corrections which had to be applied it was not to be expected that each value would be very accurate, but by averaging a large number of determinations the results obtained were quite satisfactory.

In Table II is given a typical set of corrected values of constants. Only the first nine lines are included for brevity. The terms in the last column are proportional to NxB_{ij}, and since x remained constant at 10 cm throughout the experiments, to NB_{ij}. These values were then plotted on semi-logarithmic paper against the term numbers of their corresponding lines, one curve being made for each vapor density. Nine of these curves were plotted on one sheet, and nine on another. The two resulting sets

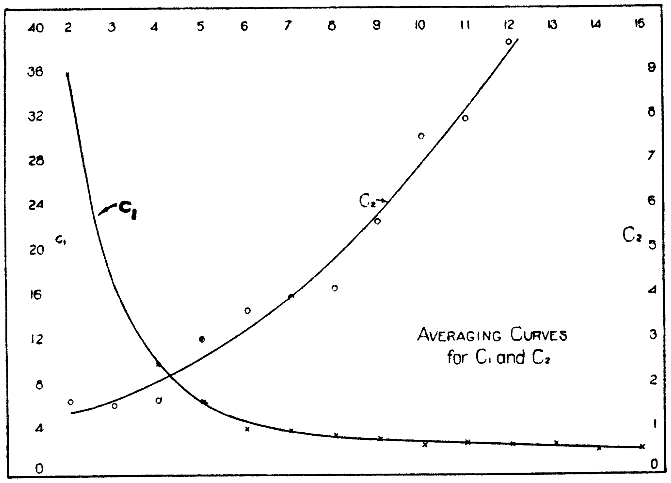

Fig. 4. Curves connecting c_1 and C_2 with term number, used to correct individual values by comparison with their neighbors.

TABLE II

Plate 26a. Spectrum 8.

Line	c_1	C_1	C_2	C_1/C_2	$\sqrt{C_1/C_2}$	$\sqrt{(C_1/C_2)}/\lambda_0$
2	35	5.0	2.0	2.5	1.58	4.78×10^{-4}
3	19	.645	2.5	.258	.508	1.79
4	13	.333	3.1	.107	.327	1.22
5	9.0	.190	3.8	.050	.224	.86
6	6.5	.090	4.8	.024	.155	.61
7	5.2	.088	6.0	.0147	.121	.48
8	4.2	.071	7.4	.0096	.098	.39
9	3.5	.059	9.0	.0065	.081	.33
10	3.2	.054	10.8	.0050	.070	.29

of approximately parallel curves were used to make two average curves, since all should presumably have the same shape, being merely displaced up or down on the $\log_{10} NB_{ij}$ axis due to their different N values. The two resulting average curves were seen to be practically identical. The average of the two was then fitted to each individual curve of the two bands, and the anti-logarithm of the end of each found, giving the relative value of N for that curve. This procedure seemed legitimate, since the results showed on the average no decrease in relative probability of the higher members with increasing vapor density. All the values of kNB_{ij} (k = proportionality factor) measured, up to the tenth line, are given in Table III, together with the corresponding values of N for each vapor density as found by the method outlined above. This would seem to be a very sensitive and accurate means of determining relative atomic vapor densities at high temperatures. It will be noted that the variation in vapor density was approximately four and one-half fold. The lowest density was taken as unity.

TABLE III

Spectrum	N (relative)	Values of kNB_{ij} for the various lines 2	3	4	5	6	7	8	9	10
25b11	1.00	2.44	1.01							
28b6	1.33	3.09	1.15	.77	.57	.41	.34	.29	.25	
25b10	1.78	5.05	1.68	1.04	.74	.54				
25a8	1.86	4.50	1.62	1.10	.78	.55	.45	.40	.35	.32
26a8	1.86	4.78	1.79	1.22	.86	.61	.48	.39	.33	.29
28b7	2.03	4.78	1.85	1.18	.83	.62	.51	.42	.36	.33
25b9	2.08	5.25	1.92	1.27	.88	.59	.52	.46	.40	.31
25a9	2.11		1.83	1.27	.94	.67	.57	.50	.45	.40
25b8	2.30		2.20	1.38	1.06	.78	.57	.51	.44	.36
26a9	2.44	6.26	2.38	1.57	1.15	.85	.65	.48	.39	.35
25b7	2.50		2.60	1.64	1.08	.825	.69	.59	.50	.31
28b8	2.78		2.86	1.79	1.25	.91	.71	.58	.52	.46
25b6	2.92		3.86	2.04	1.22	.875	.73	.62	.48	.39
26a10	3.11	8.10	3.40	2.14	1.48	1.04	.75	.60	.51	.41
25b5	3.61		4.30	2.58	1.56	1.06	.88	.75	.65	.50
25a10	3.64			1.84	1.37	1.07	.97	.87	.78	.64
28b9	3.81		3.82	2.09	1.59	1.20	.99	.82	.70	.62
25b4	4.41		5.00	3.17	2.04	1.38	1.07	.92	.77	.61

After the N values had been found by applying the average curve to each individual curve, the latter were all reduced to a common vapor density by dividing each kNB_{ij} by its proper N. The various values for each line should then have been the same, so they were all added together and the mean taken. The resulting mean values were then multiplied by N again, giving the corrected form of the curve for each vapor density. The probable error for each line was calculated, and is given in Table IV, the percentage error for the lines at the two extremes being greatest, because these were most difficult to measure and hardest to correct, and also because the smallest number of determinations were made for them. These probable errors give only an idea of the variation obtained in the results of the experiment; no estimate can be given of the actual probable error until the investigation has been repeated with a spectrograph of higher resolving power.

From the final grand average the ratios of the successive values of kB_{ij} were computed, these being given in Table IV together with the final relative values of B_{ij} and those of A_{ij}, the probability of a spontaneous transition from state j to state i with the emission of radiation. The formula for A_{ij} as given by Slater[13] is

$$A_{ij} = \frac{5.46 \cdot 10^{36}}{Nx\lambda_0^4} \cdot \sqrt{\frac{C_1}{C_2}}$$

Also the ratios of successive terms for A_{ij} are given in the table.

TABLE IV

Line	λ_0	kB_{ij}	Probable error	$(B_{ij})_n/(B_{ij})_{n+1}$	$k'A_{ij}$	$(A_{ij})_n/(A_{ij})_{n+1}$
2	3303	6.85	.098	2.44	19.0	1.56
3	2853	2.81	.043	1.65	12.2	1.38
4	2680	1.70	.030	1.43	8.85	1.29
5	2594	1.19	.012	1.34	6.85	1.26
6	2543	.89	.007	1.25	5.42	1.20
7	2512	.71	.004	1.20	4.50	1.17
8	2491	.59	.006	1.17	3.83	1.14
9	2475	.505	.006	1.15	3.36	1.14
10	2464	.440	.009	1.14	2.95	1.13
11	2455	.386	....	1.13	2.61	1.13
12	2449	.342	....	1.13	2.32	1.12
13	2444	.302	....	1.12	2.07	1.12
14	2440	.270	....	1.12	1.85	1.11
15	2437	.241	....	1.12	1.67	1.11
16	2434	.215	.005	....	1.50	....

In Fig. 5 are plotted B_{ij}, A_{ij}, and the ratios of each of these for successive lines, against term number. Various attempts to extrapolate these curves to include the D-lines proved fruitless; all devices tried indicated that the probable error would be very great, due to the tremendous difference in probability between the $1\sigma - 2\pi_{12}$ jumps and the $1\sigma - 3\pi_{12}$ jumps. The different methods gave values for the ratio A_{ij1}/A_{ij2} varying between four and twelve. In Table V are listed the available experimental results and predictions of the writers mentioned above for relative values of A_{ij}. The value for the third line is taken as unity on account of the uncertainty about the D-lines in the present work, although these are usually taken as a reference. The agreement between Hoyt's theoretical predictions and the experimental results here given is evidently close. It is unfortunate that further overlapping of data does not occur, but it is hoped that the results here published will induce theoretical physicists to extend their calculations to higher members of the series. This presents certain difficulties, since the approximations made are not always valid for higher terms.

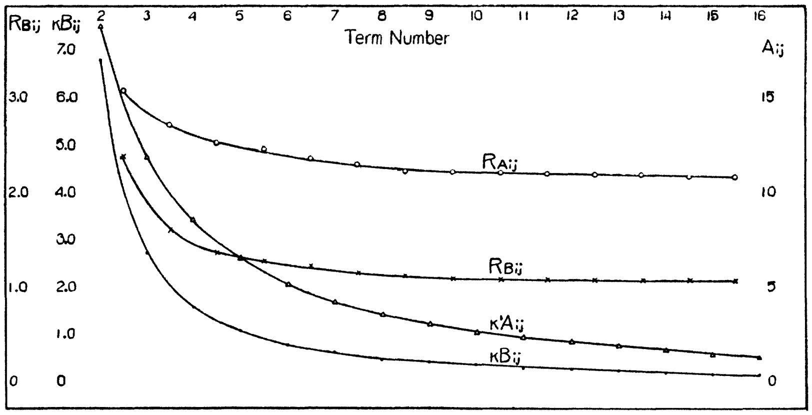

Fig. 5. Curves connecting B_{ij} and A_{ij}, as well as the ratios of successive B_{ij} and A_{ij} values, with term number.

The relative intensities of the higher members of the series and the continuous absorption beginning at the limit have been measured, and will be discussed in a later paper. The determination of absolute atomic absorption coefficients and the breadths of the lines, as obtained from the results listed above, will be given shortly in a paper to be published in collaboration with Dr. J. C. Slater, to whom I am indebted for numerous suggestions concerning the interpretation of the results listed above, and I am very grateful for having had the opportunity of discussing the present paper with him.

TABLE V

Relative values of A_{ij} given by various papers.

Line	Thomas (theory)	Hoyt (theory)	Bevan-Ladenburg (experiment)	This paper (experiment)
1	3.0-44.0	7.1	26.0	(4-12)?
2	1.67-4.2	1.57	4.22	1.56
3	1	1	1	1

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