

The Nuclear Spin of Sodium

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The alternation of intensities in absorption in the band spectrum of sodium was investigated for the purpose of determining the spin of the sodium nucleus. Measurements were confined to the (0,2) band in the ${}^4\Pi \leftarrow {}^2\Sigma$ transition, which alone is reasonably free from overlapping bands. Relative absorption coefficients for the Q branch lines, with

$J=48$ to $J=73$ inclusive, were calculated. These yielded an average value for the alternation of intensities of 1.71, the average being obtained from 5 different plates. These results agree best with the theoretical alternation ratio of 1.67 corresponding to a nuclear spin of $3/2$.

INTRODUCTION

ALTHOUGH alternation of intensities in band spectra does not offer a method of great precision in the determination of nuclear spins, the present state of knowledge makes it highly desirable that as many different methods as possible be used to determine these constants. Especially is this true for sodium, for which previous experimenters have obtained widely differing results. Hyperfine structure investigations have given $i=1/2, 1, 3/2$ for the spin.^{1, 2, 3, 4, 5, 6} The polarization of resonance radiation indicates $i=1$, according to Ellett.⁷ Band spectral observations by Loomis and Wood⁸ suggested $i \geq 3/2$.⁹ Atomic beam pattern investigations by Rabi and Cohen have recently yielded a reliable value of $3/2$ for the nuclear spin.¹⁰ Urey previously showed that the sodium nucleus obeys the Fermi-Dirac statistics.¹¹ As band spectral observations^{8, 9} appeared to disagree with the values of i obtained

by other methods, we undertook a quantitative investigation of alternating intensities in absorption in sodium bands.

In this connection it was found impossible to use the methods of Harvey and Jenkins¹² and of Van Wijk and Van Koeveringe,¹³ who obtained the alternation of intensities in the lithium bands without determining directly absorption coefficients of lines. In our case, the number of lines available for intensity measurements was too small and the deviations in line intensities produced by background irregularities were too large to use these methods. It was found necessary to measure relative absorption coefficients of lines after the manner of the work of Elliott^{14, 15} on chlorine bands and the work of Childs and Mecke¹⁶ on the acetylene bands.

APPARATUS AND PROCEDURE

The absorption spectrum was photographed in the second order of a 21-foot concave grating, having 14,500 lines to the inch and six inches wide. The photographic plates were Eastman Spectroscopic Plates Type 3J. A 500-candlepower lamp, with an arc between tungsten electrodes served as a continuous source.* The light

¹ H. Schüler, *Naturwiss.* **16**, 513 (1928).

² H. Schüler and J. E. Keyston, *Zeits. f. Physik* **68**, 174 (1931).

³ R. deL. Kronig and S. Frisch, *Phys. Zeits.* **32**, 457 (1931).

⁴ Frisch and Ferchmin, *Naturwiss.* **18**, 866 (1930).

⁵ K. Murakawa, *Inst. Phys. and Chem. Research Sci. Papers* No. 398, p. 1-12 (Dec. 1932).

⁶ C. M. Van Atta and L. P. Granath, *Phys. Rev.* **44**, 60 (1933); **44**, 935 (1933).

⁷ Heydenburg, Larrick and Ellett, *Phys. Rev.* **40**, 1041 (1932).

⁸ F. Loomis and R. Wood, *Phys. Rev.* **32**, 223 (1928).

⁹ A. Ellett, *Phys. Rev.* **35**, 594 (1930), footnote.

¹⁰ I. Rabi and V. Cohen, *Phys. Rev.* **43**, 582 (1933).

¹¹ H. Urey, *Phys. Rev.* **38**, 1074 (1931).

¹² A. Harvey and F. Jenkins, *Phys. Rev.* **35**, 789 (1930).

¹³ Van Wijk and Van Koeveringe, *Proc. Roy. Soc.* **A132**, 98 (1931).

¹⁴ A. Elliott, *Proc. Roy. Soc.* **A123**, 629 (1929).

¹⁵ A. Elliott, *Proc. Roy. Soc.* **A127**, 638 (1930).

¹⁶ W. Childs and R. Mecke, *Zeits. f. Physik* **64**, 162 (1930).

* This was the Point-o-Lite lamp manufactured by James G. Biddle, Philadelphia, Pa.

from the incandescent electrode was focussed by means of a condensing lens, placed between the lamp and the absorption tube, onto the slit of the spectrograph.

The iron absorption tube is shown diagrammatically in Fig. 1. Nitrogen gas, freed from

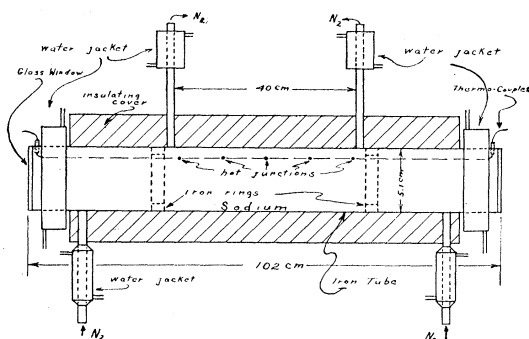


FIG. 1. The absorption cell.

oxygen and water vapor, was admitted into the absorption tube through two side pipes at the ends of the tube, while two more centrally located pipes served to draw it away. Metallic sodium could be placed in a 40 cm central portion of the tube and its vapor kept in that region by the flow of nitrogen gas from the ends of the tube towards the central outflow pipes. Two cylindrical iron rings were placed inside the tube (see Fig. 1) to assist in keeping the gaseous and liquid sodium confined in the central region. Glass windows were cemented to each end of the tube with de Khotinsky cement. Two chromel resistance coils, imbedded in alundum cement and asbestos, heated the tube electrically. One of the coils heated the tube along its whole length, while the other was short-circuited along the 40 cm central portion and heated the ends. By adjusting the current in each coil to the proper value, it was possible to obtain a uniform temperature in the 40 cm central portion of the tube, to which the sodium vapor was confined. Five iron-constantan thermocouples were strung through the tube with their hot junctions spaced at 10 cm intervals in the central 40 cm column. The heating of the tube was so regulated that the thermocouples showed a variation in temperature of only about two degrees and also no more than a two-degree variation in the course of the

thirty-minute exposures. The suitable working temperature for the sodium vapor was found to be 347°C. Different nitrogen gas pressures up to atmospheric pressure were used in order to study the effects of possible line broadening on intensity ratios.

A comparison iron spectrum, the absorption spectrum, and sets of calibration marks were photographed at the top, middle and bottom of the plate respectively. A screen placed in front of the plate in its mounting, was used to give the three different exposures on the plate. The screen was supported by the arrangement shown diagrammatically in Fig. 2, and could be moved up

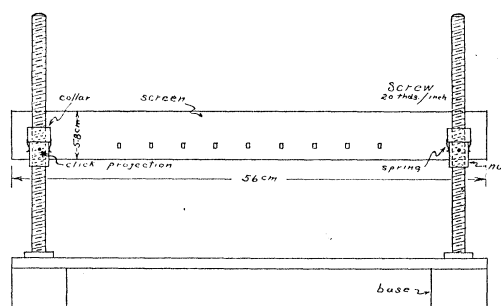


FIG. 2. The photographic plate screen.

and down by a pair of clicking nuts. Small rectangular openings in the lower half of the screen served to produce sets of calibration marks on the plate, a set of different wave-length for each opening. This was accomplished by moving the plate in its rack a few mm between exposures for density marks and keeping the screen stationary. To produce density marks of different relative intensities for each exposure, a tungsten ribbon filament lamp and rotating copper oxide screens were used according to the procedure described by Harrison.¹⁷ The plates were microphotometered on a Moll microphotometer.

CALCULATION OF RESULTS

Three sets of calibration marks in the region of the band under investigation were microphotometered, yielding three characteristic curves for each plate, each corresponding to a different wave-length. The curves for plate C are shown

¹⁷ G. R. Harrison, J. O. S. A. and R. S. I. **18**, 492 (1929).

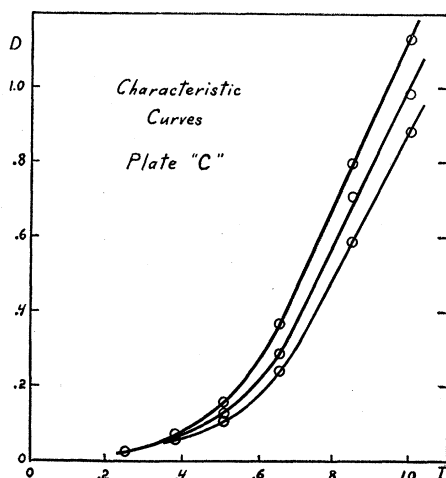


FIG. 3. Characteristic curves for Plate C.

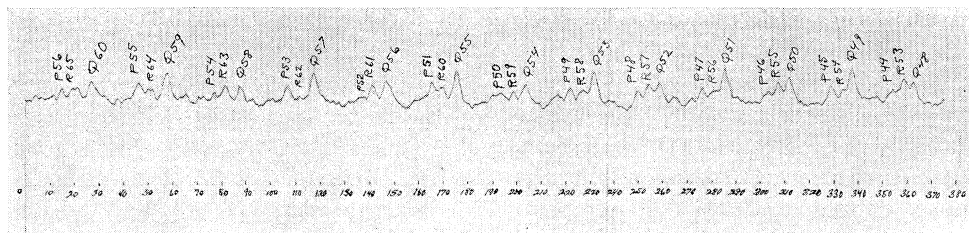
in Fig. 3. The absorption band spectrum was also microphotometered, a portion of a tracing being shown in Fig. 4.

The density D of any point on the plate is given by $D = \log_{10}(F_m/F)$, where F_m is the height of the clear plate deflection on the microphotometer curve above the dark point line, and F is the height of the given point above the dark point line. The characteristic curves, which represent a plot of D against I , where $I = \log_{10} i$ (i is here the relative intensity), could then be used to translate densities into relative intensities.

We notice that the band lines occur in groups of three with an irregular background between each group. The designations of the lines as assigned by Loomis and Wood⁸ are shown in Fig. 4. Measurements were confined to the (0,2) band in the ${}^1\Pi \leftarrow {}^1\Sigma$ transition, which alone was sufficiently free from overlapping bands to be used for intensity measurements. It was found that,

besides the P , Q and R branch lines of the band, irregularities occurred throughout the spectrum. These could not be attributed either to the light source or to the optical system, since the same irregularities appeared on the microphotometer tracings from a plate by Loomis and Wood,⁸ who used a different source (carbon arc) and grating. All attempts to systematize these irregularities or to trace them to impurities or to any overlapping Na_2 bands failed. Since these apparently random irregularities could underlie the band lines and thus affect their intensities, the problem of determining the true value of the latter became a difficult one.

Of the three branches, the Q branch is the most intense and hence it is affected least by background irregularities. Moreover, the range over which the Q lines were resolved from the P and R companions was larger than the corresponding range for either the P or R lines. Therefore, intensity measurements were limited to the Q lines, with $J=48$ to $J=73$ inclusive. For $J < 48$, the Q line was not sufficiently resolved from its companions to warrant intensity measurements. For $J > 73$ the background irregularities became so large that large errors would be introduced into intensity measurements. The following method was devised to compensate for the disturbing effect of background irregularities: it was assumed that the background irregularities can be treated as a random phenomenon and that the background occurring between band line groups is a representative sample of the entire background. The heights of the background occurring between each two band line groups were measured at small regular intervals yielding about 7 readings in each case, and the average of these was taken as the height of a representative background point between two such groups. To prove



that averaging background heights (galvanometer deflections) is equivalent to averaging background intensities, we calculated in several instances the intensity corresponding to each reading and averaged the intensities. In each case the same value was obtained for the average point as by the first method. Since the first method is much the shorter one, it was adopted throughout the calculations.

Let the calculated deflection corresponding to each such average point be F_0 . A plot of $\log_{10} F_0$

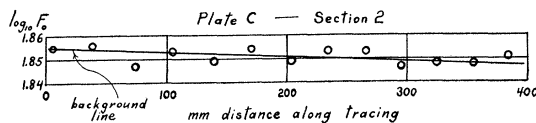


FIG. 5. Plot of $\log_{10} F_0$ against position along tracing.

against position along the tracing was made for each microphotometer tracing. Fig. 5 shows one such graph. It was found that in every case a straight line drawn through the plotted points was the best representative simple curve for the background density distribution. An interpolated value for the background density, D_0 , could then be obtained from the graph for the background occurring directly under each absorption line. This method of calculating the background under a line removes a systematic error which would result if we referred the line intensities to the lowest points in the background. The density at the peak of each absorption line is given by $D = \log_{10} F_m/F$ where F_m and F are defined as above, and F refers to the line peak.

The calculation of intensities from corresponding densities was carried out with the aid of three characteristic curves which had been obtained for each plate. Thus, for two of the plates these curves were obtained for the wave-lengths of 4985, 5035 and 5085A, whereas the lines whose intensities were measured are located between 5019 and 5039A. To each curve was fitted an equation of the type: $D = a + bK + cK^2$, where $K = I - \text{constant}$, and then the values of a , b and c were interpolated for the wave-length of each absorption line whose intensity was to be found. By this method values of I and I_0 , corresponding to values of D and D_0 respectively, were obtained for each absorption line in question. We desire in

the case of each line, the quantity

$$\alpha = I_0 - I = K_0 - K. \quad (1)$$

This method of analytical interpolation for a value of α for each absorption line was checked by graphical interpolation for α directly from the three characteristic curves.

Further calculations follow from the following theoretical arguments: the intensities of the incident and transmitted light in absorption are given by

$$i_\nu = i_0 e^{-\beta_\nu l} \quad (2)$$

where i_0 is the intensity of light in the background, i_ν is the intensity of light in the absorption line at wave-length ν , β_ν is the coefficient of absorption at wave-length ν , and l is the thickness of the absorbing layer, which is a constant for all the lines.

The coefficient, β_ν , will have a different form, depending on whether the shape of the line is determined by Doppler or "Dispersion" broadening.¹⁸ For absorption at the center of the line, we have

$$i = i_0 e^{-\beta l} \quad (3)$$

where all quantities are referred to the center of the line. It can be shown, irrespective of whether the shape of the line is determined by Doppler or "Dispersion" broadening, that the coefficient of absorption at the center of the line, β , becomes directly proportional to Einstein's coefficient of absorption and the number of molecules in the initial state.¹⁸ If the observed intensity of the peak of the absorption line be taken as a measure of the true intensity, i , of the center of the line, we have for the center of the line

$$\beta l = \log_e 10 (\log_{10} i_0 - \log_{10} i). \quad (4)$$

Letting $\alpha = \log_{10} i_0 - \log_{10} i = I_0 - I = K_0 - K$, we see that α will obey the same proportionality relation as that stated above for β . More explicitly, we have

$$\alpha \propto \hbar \nu_{mn} B_{mn} g_m \exp(-E_m/kT). \quad (5)$$

Using Einstein's coefficient of spontaneous emission, A_{nm} , instead of B_{mn} , we have from the relation:

$$B_{mn} = A_{nm} (g_n/g_m) (C^3/8\pi\hbar\nu^3) \quad (6)$$

¹⁸ R. Ladenburg and Levy, Zeits. f. Physik 65, 189 (1930).

that

$$\alpha \propto \nu^{-2} A_{nm} g_n \exp(-E_m/kT). \quad (7)$$

The theoretical relative values of the intensity factor $A_{nm} g_n$ for the lines in a band are given for our case by Dennison.¹⁹ For the Q lines of our band, the intensity factor is $c(2J+1)g_i$ where c is a constant for all the lines in the branch and g_i is the statistical weight factor due to the spin of the nucleus. Variation in ν over the range of lines measured is very small. Therefore we will assume that, very nearly, we have

$$\alpha \propto (2J+1)g_i \exp(-E''/kT), \quad (8)$$

where E'' is the rotational energy of the lower state of the absorbing molecule, which is usually given as:

$$E'' = BhcJ(J+1)/kT + DhcJ^2(J+1)^2/kT. \quad (9)$$

The values for B and D are given by Loomis and Wood⁸ and are: $B = 0.15255$ and $D = -0.5954 \times 10^{-6}$. For our purposes the D term may be neglected. We may then write:

$$\alpha = C(2J+1)g_i \exp[-BhcJ(J+1)/kT] \quad (10)$$

where C is a constant for all the lines in question. This equation is equivalent to

$$\begin{aligned} [\alpha K_{00}/(2J+1)] \exp[BhcJ(J+1)/kT] \\ = Cg_i K_{00}, \quad (11) \end{aligned}$$

where K_{00} is a constant used for purposes facilitating computation.

Letting $Cg_i K_{00} = M$, we can obtain from Eq. (11) one set of experimentally observed values of M for the strong lines and another set for the weak lines, each M being computed from the experimentally known values of α and T . The calculated values of M for all plates are given in Table I. An average of all the M 's for the strong lines, $M_A(\text{strong})$, is considered as the best value for $Cg_i K_{00}$ for the strong lines, and similarly $M_A(\text{weak})$ for the weak lines. It is clear that:

$$\frac{M_A(\text{strong})}{M_A(\text{weak})} = \frac{g_i(\text{strong})}{g_i(\text{weak})} = \frac{i+1}{i}, \quad (12)$$

i.e., $M_A(\text{strong})/M_A(\text{weak})$ gives us the best value for the alternation of intensities. From this

¹⁹ D. Dennison, Phys. Rev. **28**, 318 (1926).

TABLE I.

J	B	C	D	D'	F	G
48	0.276	0.261	0.357	0.330	0.417	0.420
49	.455	.493	.633	.639	.678	.698
50	.397	.411	.448	.474	.510	.545
51	.491	.446	.629	.594	.736	.711
52	.322	.250	.352	.359	.435	.410
53	.522	.517	.605	.687	.689	.793
54	.448	.355	.337	.478	.481	.504
55	.574	.509	.638	.626	.677	.804
56	.412	.340	.422	.495	.502	.475
57	.459	.472	.606	.601	.739	.710
58	.274	.231	.316	.349	.337	.350
59	.534	.441	.626	.664	.646	.795
60	.379	.276	.415	.405	.541	.572
61	.477	.464	.522	.592	.703	.782
62	.321	.338	.293	.382	.478	.473
63	.585	.550	.660	.749	.826	.941
64	.178	.197	.219	.224	.284	.316
65	.551	.432	.561	.594	.712	.738
66	.205	.197	.237	.277	.447	.319
67	.591	.502	.586	.805	.760	.892
68	.323	.322	.239	.418	.365	.393
69	.410	.334	.524	.537	.639	.630
70	.274	.240	.271	.285	.301	.305
71	.542	.404	.501	.579	.623	.718
72	.299	.242	—	.308	.323	.420
73	.542	.503	—	.544	.588	.752

TABLE II.

Plate No.	N ₂ Pressure	Temperature	$(i+1)/i$	Probable Error (P.E.)
B	2.5 mm	347°C	1.64	± 0.09
C	27.4 mm	348°C	1.66	$\pm .08$
D †	103 mm	346°C	1.77*	$\pm .08$ (estimat.)
F	185 mm	347°C	1.66	$\pm .07$
G	185 mm	348°C	1.81	$\pm .08$

Average = 1.71

* Note: The value, 1.77, is an average obtained from two different tracings of the same plate, D , which yielded 1.82 ± 0.09 and 1.72 ± 0.08 respectively. Since this plate lacked a comparison iron spectrum, it presented special difficulties in alignment for microphotometry. Hence, the plate was microphotometered twice.

† Lines $J=72$ and $J=73$ were not measured on the first tracing of plate D .

i , the spin of the sodium nucleus, is found. Calculated values of $(i+1)/i$ are listed in Table II. In Fig. 6 is shown a plot of M against J for plate C , the horizontal straight lines representing $M_A(\text{strong})$ and $M_A(\text{weak})$ respectively for that plate.

DISCUSSION

Undoubtedly, a serious possible source of error in our calculations is the assumption that the observed intensity at the peak of an absorption

line is a measure of the true intensity at the center of the line. The finite slit widths in our optical system and the finite resolving power of the grating both influence the observed intensity and change the observed shape of the line from its true shape. Especially may this effect be disturbing in the case of absorption lines, whose shape varies with the percentage of the light absorbed. This effect will become more important as the amount of absorption increases. However, when we consider Table I, and Fig. 6, we notice

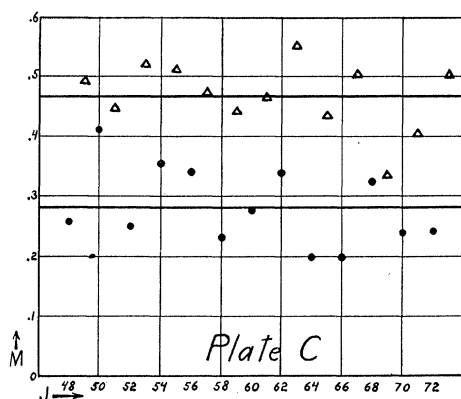


FIG. 6. Plot of M against J for Plate C.

that M (odd lines) is a good constant over our range of observations in spite of the fact that the magnitude of the absorption coefficients varies from one end of the graph to the other by a factor of 2.5. This, obviously, would not be the case if the above-mentioned source of error were present. That M (even lines) is not as good a constant as M (odd lines) is explained by the fact that background irregularities introduce a larger variation into the observed values of the α 's for the weak than for the strong lines, and that smaller absorptions are known with smaller precision.

Another serious possible source of error in our calculations is the disturbing effect of background irregularities. Our method of construction of an average background line, presupposes that background irregularities occur in a random fashion. It is clear that the true relative absorption coefficients of the lines will differ from those calculated by this method, depending on whether the actual background under the absorption line happens to be lower or higher than the average

background line, and the deviations from the true values will be random if the background irregularities occur in a random way. This partly accounts for the scattering of the points in Fig. 6. Other effects tending to scatter the observed values from the average are grain in the plate, dust particles, developer effects, galvanometer vibrations and other limitations in accuracy inherent in photometric determinations of intensities. Since these effects may be treated as largely random, we see that, as far as such errors go, the large number of observations available makes the final average much more reliable than the ratio of intensities as calculated from a single pair of lines on a single plate. The P.E. measure obtained for each plate is a good measure of the reliability of the mean for that plate as far as accidental and random errors go. The reliability measure of the mean for all plates should not be much better than that for a single plate, since the effect of background irregularities is the same on all plates. Hence, we consider a P.E. = ± 0.08 to be a good measure of the reliability of the mean for all plates, as far as random errors are concerned. We must, however, call attention to the fact that the values of M (even lines) show a trend in Fig. 6. That this trend is not real and is the effect of a random distribution of errors is suggested by the fact that M (odd lines) shows no such trend; and we would hardly expect the odd and even lines to follow different laws. Still, the possibility remains that the trend is produced by a systematic background disturbance affecting mainly the even lines. In that case, the reliability of our results would be considerably less than that indicated by the above P.E. value.

RESULTS

The average value for $(i+1)/i$ computed from all the plates is 1.71 with a P.E. = ± 0.08 , assuming no systematic error. Since, as pointed out in an earlier paragraph, there is a possibility of systematic errors, we estimate the reliability of the above ratio to be considerably less than that indicated by the above P.E. The above average value agrees best with the value 1.67, the theoretical value corresponding to a spin of $3/2$ for the sodium nucleus. We conclude therefore from these results that the most probable value of the

spin is $3/2$, but that the values of 1 and 2 are not excluded as highly improbable.

In addition, it may be stated that the observation of Urey,¹¹ that the sodium molecule obeys the Fermi-Dirac statistics, has been confirmed by our present investigation. In all other cases, where both the spin of the nucleus and statistics are known, it has been found that in the case of nuclei with integral spins, the Bose-Einstein statistics are obeyed, while in the case of nuclei with half-integral spins, the Fermi-Dirac statistics are obeyed. Our results are in agreement with this experience.

In conclusion, I wish to express my sincere appreciation to Professor Harold C. Urey, who inspired this investigation, for his constant help and advice throughout this research. I also wish to thank the Physics Department at Columbia University for the use of their grating, and to express my appreciation to Dr. Gorman and Mr. Shriver of New York University for their work in making the microphotometer tracings, and to Professor F. W. Loomis of the University of Illinois for the loan of his note-books covering the analysis of the spectral region used in this investigation.

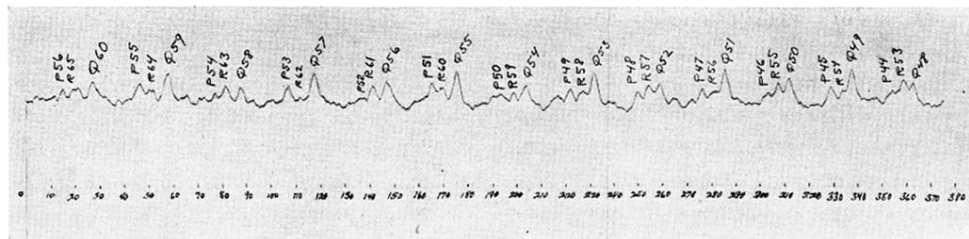


FIG. 4. Portion of microphotometer tracing of absorption band.