HYPERFINE SPLITTING

OF THE NORMAL s STATE OF SODIUM

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By

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PREFACE

It has been observed that many spectral lines, especially those of the heavier atoms, show a narrow fine structure with separations of the order of one wave-number unit. These separations are very much smaller than those of the ordinary multiplet structure of heavy atoms, and for this reason these spectra are said to show <u>hyperfine structure</u>.[1] There are two types of hyperfine structure (hereafter to be abbreviated hfs) to be distinguished from each other. First, there is a hfs due to a nuclear magnetic and mechanical moment and, second, a hfs due to the different isotopes of the same chemical element.[2] There exists hfs of the first type in the D lines of sodium and it is the purpose of this thesis to determine the separation of the two components of both of the D lines. This separation was determined by experimental means as well as from theoretical considerations. Correlation between theoretical and experimental hfs separations is then made.

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[1] Linius Pauling and Samuel Goudsmit, <u>The Structure of Line Spectra</u>, p. 202.

[2] Harvey Elliott White, <u>Introduction to Atomic Spectra</u>, p. 353.

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The author wishes to take this opportunity especially to thank Dr. S. W. Eager, under whose direction this project was completed, and also Dr. A. V. Pershing, who personally supervised the investigation.

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PART I

EXPERIMENTAL DETERMINATION OF HFS IN THE SODIUM LINES

For experimental investigation of hfs of the sodium lines the Fabry-Perot interferometer was employed. Before discussing the actual measurements, the method used must be clarified. First let us consider the method used to find the separation of two spectral lines relatively near one another, e.g., the D lines of sodium. The apparatus used is shown set up in figure 1.

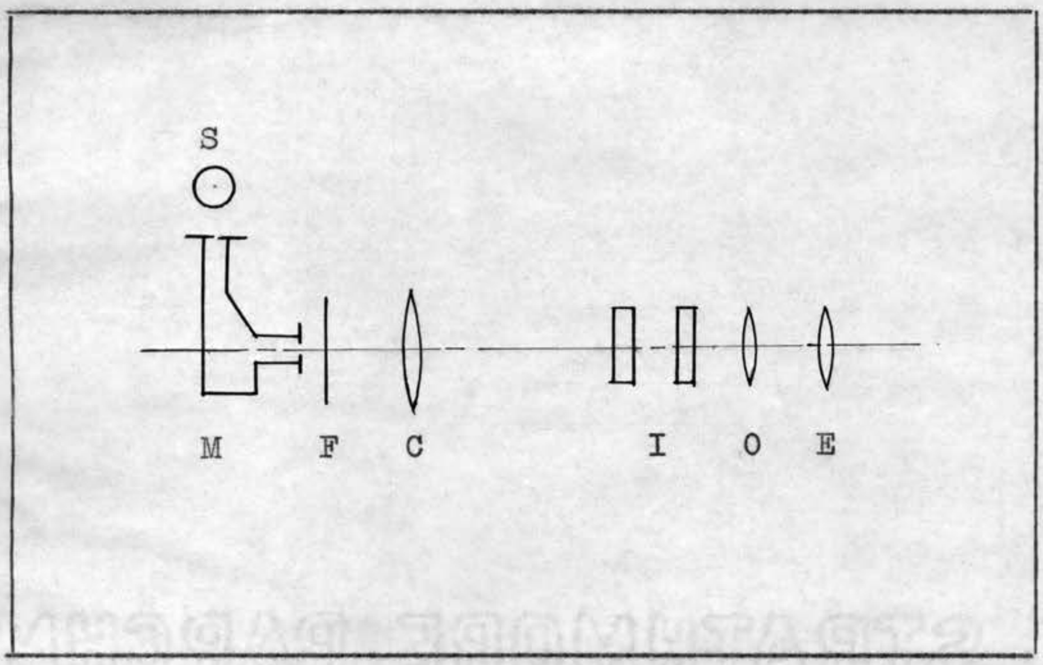

Figure 1.

In figure 1, S is the source, a General Electric Sodium Lab-Arc; M, a rapid setting monochrometer used to obtain light as near one wave length as possible; F, a Kodak Wratten filter number 67, renders the light still more monochromatic; C, a collimating lens; I, the half silvered parallel plates of the Fabry-Perot interferometer; and O and E the objective lens and eyepiece, respectively, of the observer's telescope. The equation from which $\Delta\lambda$, the wave-length separation between the sodium D lines, is determined follows:

$$\Delta\lambda = \lambda_1 - \lambda_2 = \frac{\lambda_1 \lambda_2}{2\,ut\cos\theta} \qquad (1)$$

Here λ_1 and λ_2 are the wave lengths of the D lines expressed in centimeters, $\lambda_1 > \lambda_2$, u the index of refraction for air, t the difference in plate separations, measured in centimeters, between successive coincidences of the fringe systems, and θ the angle between the incident ray and the axis of the interferometer. If λ_1 and λ_2 are very nearly the same and if we confine our attention to the rings near the center of the fringe system, we can say

$$\Delta\lambda = \frac{\lambda_1^2}{2\,ut} \qquad (2)$$

To find the wave number distance $\Delta\nu$ corresponding to the $\Delta\lambda$ in equation (2), we take the relation between ν and λ,

$$\nu = \frac{1}{\lambda}$$

λ being in centimeters, and differentiate it, obtaining

$$\Delta\nu = -\frac{\Delta\lambda}{\lambda^2}$$

Substitution in equation 2 gives

$$\Delta \nu = - \frac{1}{2\,ut} \qquad (3)$$ [1]

For our purpose the - sign may be neglected. From the last expression it follows that the wave number difference is inversely proportional to the plate separation between coincidences. Consequently, the plate separation between two successive coincidences of the hyperfine fringes of each D line must be considerably greater than the separation between coincidences of the D line fringes themselves since the former are much closer together.

The following sketches in figure 2 indicate the relative positions of the fringes formed by the two componets of each of the D lines. Here D1-0, D1-1 and D2-0, D2-1 are the components of the D1 and D2 lines respectively. Since the D2 line is twice as intense as the D1 line, its components are drawn twice as heavy as the D1 components. Positions are shown when the fringes are in phase, out of phase by $\pi/2$ radians, out of phase π radians, and then back in phase again. In other words, fringes are shown at intervals of 1/4 a beat length, the beat length L being the distance betwen successive coincidences. The 3 $\pi/2$ position is not shown since it falls beyond the range of the interferometer. If the two mirrors were in contact, the fringes would be in phase as shown in the 0 position in figure 2. When the plate separation is 1/4 the beat length L, the fringe system would be as shown for the $\pi/2$ position. D1-1 has here advanced 1/4 the way to the original position of the next D1-1 fringe, while D2-1 has also advanced 1/4 the way to the original position of the next D2-1 fringe. As shown in the π

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[1] F. A. Jenkins, and H. E. White, <u>Fundamentals of Physical Optics</u>, pp 100-101

position, the D1-1 and D2-1 fringes have now advanced 1/2 the distance to the original positions of the next D1-1 and D2-1 fringes, respectively, since the plate separation is L/2, 1/2 the beat length. Since $\Delta\nu$, the wave number distance between D1-0 and D1-1 and between D2-0 and D2-1, is quite small, L will be quite large. As plate separation

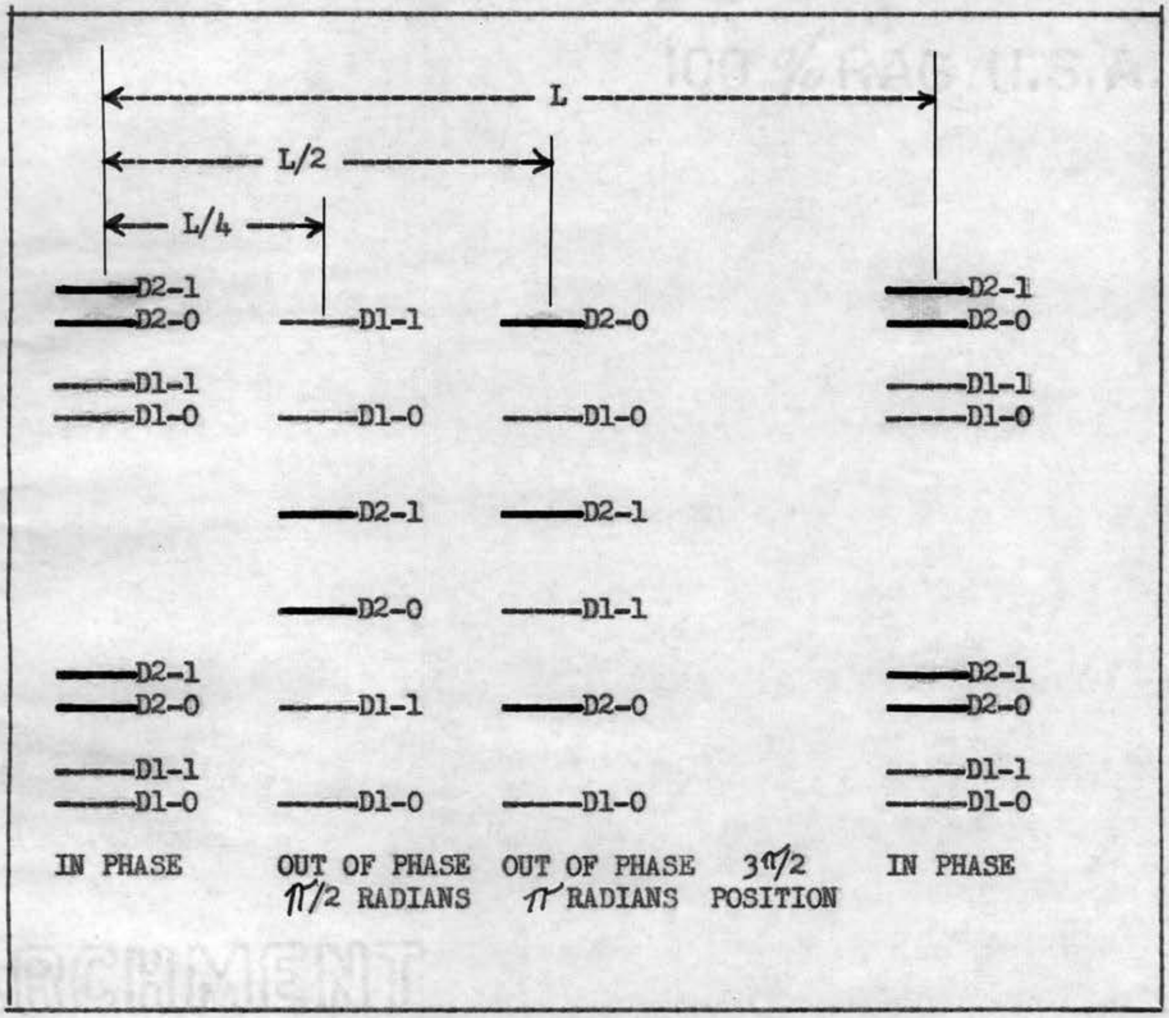
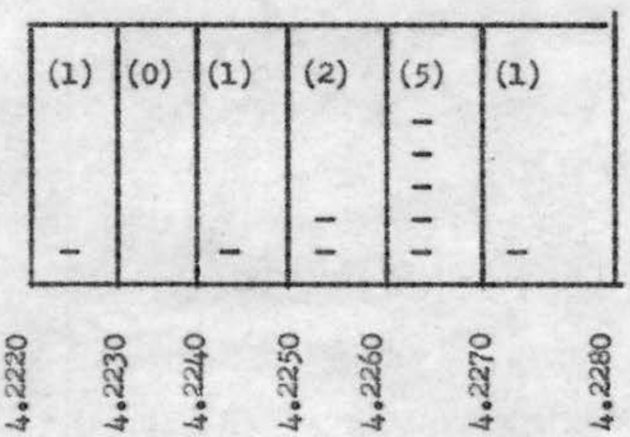


Figure 2.

increases, distance between fringes decreases. This coupled with the fact that the fringes in the $\pi/2$ and π positions are very evenly spaced, should lead to a very uniform distribution of fringes very close together in the $\pi/2$ and the π positions. We might suspect that the fringes would be "smeared". That is to say, the field of view apparently would be uniformly illuminated except near the center where fringes should be discernible in the region of maximum fringe separation. The plate separation at the $\pi/2$ position must be multiplied by 4 to give the beat length L, which is equivalent to t in equation 3. Similarly, for the π position, t is equal to twice the distance between the plates. With these modifications, $\Delta\nu$ can be computed for both the π and the $\pi/2$ positions. The mean of these two values will then give the hyperfine separation of the D line components in cm^{-1}. Careful observation of the fringe systems as the plate separation was gradually increased from a minimum value resulted in the discovery of "smeared" fringes in the vicinity of 2.139 cm and 4.189 cm. These are scale readings and not actual mirror separations. Obviously these readings correspond to the $\pi/2$ and π positions respectively. These positions must now be accurately found and the actual mirror separations determined. $\Delta\nu$ can then be found by means of equation 3. These preliminary positions were determined with the filter removed. With the filter in position, the $\pi/2$ position was more carefully investigated. The position in which maximum "smearing" of the fringes occurred was located at the scale reading of 2.240 cm. Further investigation of this region was postponed until the π position was accurately determined. The scale settings of the four best positions in the second region where the "smearing" of fringes was observed were recorded as follows: (1) 4.252 cm, (2) 4.229 cm, (3) 4.197 cm, (4) 4.171 cm. Hereafter all scale readings will be in centimeters so the units will be omitted. Checking between positions 1 and 2 it was decided that the smearing was better in position 2. Between positions 3 and 4, the latter was eliminated. Deciding between the two intermediate positions, position 2 was finally chosen over number 3. Careful observation showed that the position of maximum smearing (hereafter to be abbreviated the maximum) was between the limits 4.2220 and 4.2280. Within this region, ten observations of the maximum were observed and recorded:

4.22503
4.22623
4.22269
4.22686
4.22550
4.22706
4.22606
4.22617
4.22630
4.22410

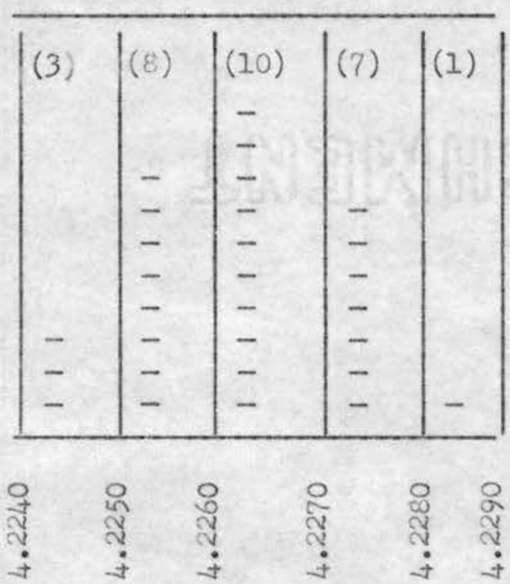
The above mentioned region was divided into six intervals (cells) of 0.001 cm separation and the readings falling into each cell were counted as shown below.



From this plot it is apparent that the maximum is between 4.2260 and 4.2270. Taking this cell and two on each side, twenty readings between these limits (4.2240 and 4.2290) were recorded on page 7.

4.22566
4.22726
4.22492
4.22771
4.22403
4.22692
4.22594
4.22725
4.22585
4.22765
4.22618
4.22812
4.22542
4.22642
4.22592
4.22764
4.22626
4.22744
4.22582
4.22686

These readings were counted for each cell and added to those previously counted for these cells. The plot follows:



Since it is now highly probable that the maximum is between 4.2260 and 4.2270, the ten readings lying between these limits were recorded again and averaged.

4.22623
4.22686
4.22606
4.22617
4.22630
4.22692
4.22618
4.22642
4.22626
4.22686

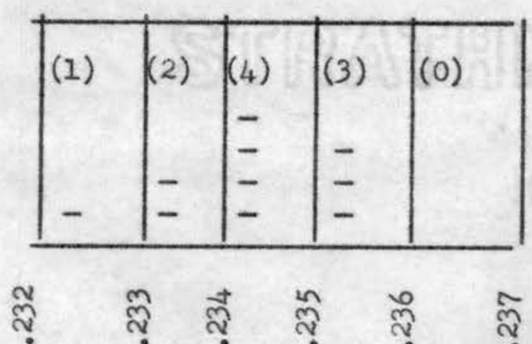
Mean = 4.226426 cm

This position is the scale reading and not the actual distance between the mirrors. With the mirrors just touching, the scale reading was 0.172750 cm. Subtracting this "O" reading from the mean position previously determined, the mirror separation at the π position was determined as 4.053676 cm.

Since the π position occurs with a plate separation twice as large as that for the $\pi/2$ position, one half the plate separation found above should give the plate separation for the $\pi/2$ position. When added to the "O" position, this should give the scale reading where "smearing" occurs in the $\pi/2$ position. This was done. The scale reading thus found was 2.199588 cm, roughly, 2.200 cm. This probable maximum position was compared with that previously located at 2.240 cm. All observations in this position were conducted with the filter in position, while those at the π position were made with the filter removed because it cut down the fringe intensity too much. After observing the two maxima nearest 2.200 and 2.240, it was decided that the one in the vicinity of 2.240 was the better. Five readings of this maximum were taken and recorded.

2.232
2.236
2.237
2.233
2.236

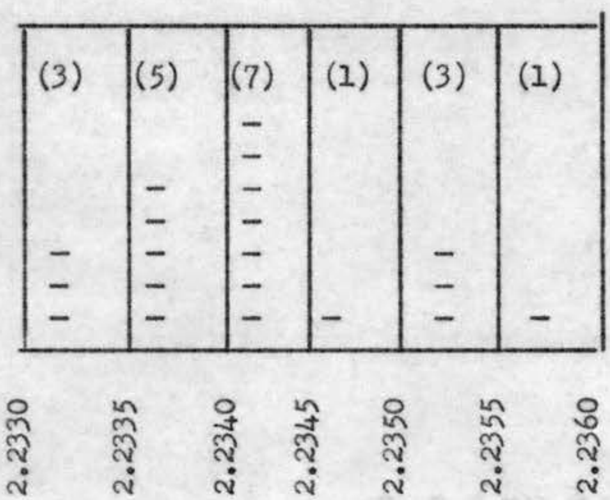
These readings show the maximum to be between the limits 2.232 and 2.237. Ten readings between these limits were taken and plotted in cells of 0.001 cm separation.



2.23280
2.23423
2.23440
2.23594
2.23356
2.23594
2.23445
2.23498
2.23504
2.23378

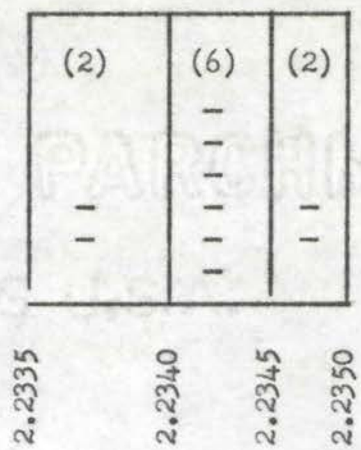
These results have narrowed the range so it is bounded by scale readings of 2.2330 and 2.2360. This range was divided into six equal intervals of 0.0005 cm. separation and twenty readings were recorded and plotted.

2.23423
2.23339
2.23317
2.23322
2.23443
2.23501
2.23533
2.23419
2.23558
2.23409
2.23473
2.23357
2.23426
2.23365
2.23434
2.23372
2.23421
2.23390
2.23533
2.23393



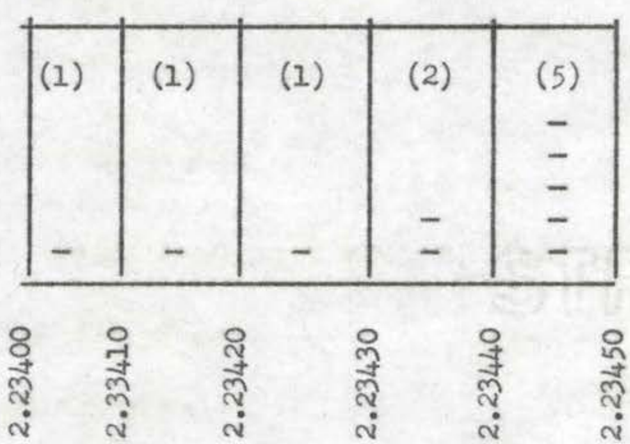
These results have indicated that the maximum lies between the limits 2.2335 and 2.2350. Ten readings between these limits were plotted in cells of 0.0005 cm separation.

2.23385
2.23431
2.23404
2.23450
2.23417
2.23399
2.23481
2.23436
2.23423
2.23442



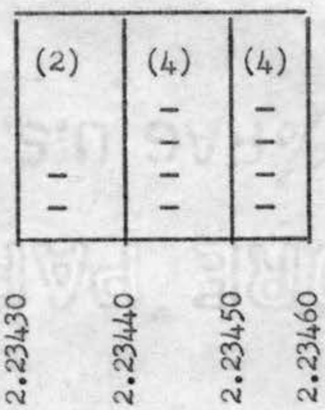
This plot verifies the result of the preceding plot in showing the maximum to be between scale positions 2.2340 and 2.2345. This interval was accordingly divided into five cells of 0.0001 cm separation and 10 readings were recorded and evaluated by plotting.

2.23445
2.23439
2.23442
2.23407
2.23446
2.23413
2.23448
2.23442
2.23443
2.23436



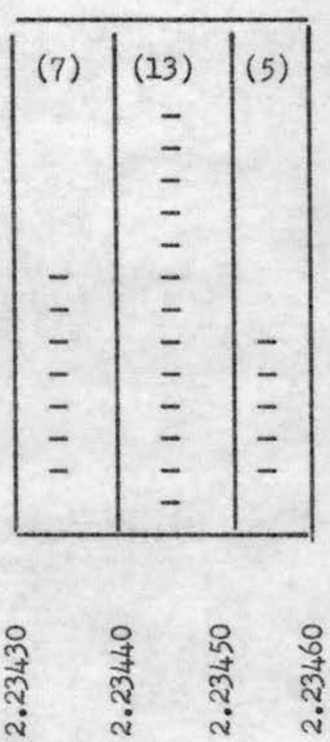
Ten observations between the more confining limits, 2.2343 and 2.2346 were taken and plotted.

2.23430
2.23459
2.23441
2.23444
2.23448
2.23453
2.23451
2.23454
2.23436
2.23446



Since the readings are very evenly distributed the maximum must be in one of these three cells. All the previously obtained readings lying in this range were recorded again and a new plot, including the above readings, was made between the same limits.

2.23434
2.23431
2.23436
2.23439
2.23436
2.23440
2.23445
2.23443
2.23442
2.23445
2.23442
2.23446
2.23448
2.23443
2.23450



The maximum is definitely between 2.23440 and 2.23450. To the thirteen readings already recorded as falling in this region, seven new ones were taken and added. The average of these twenty readings was taken as the scale reading at the $\pi/2$ position. The thirteen old readings plus the seven new ones are recorded below.

2.23443
2,23442
2.23446
2.23448
2.23443
2.23442
2.23440
2.23445
2.23445
2.23441
2.23444
2.23448
2.23446
2.23449
2.23441
2.23447
2.23449
2.23446
2.23445
2.23448

The zero position was then redetermined and found to be 0.183985. Subtraction of the "0" position from the mean scale reading at the position of the maximum gives the plate separation as 2.050464 cm at the $\pi/2$ position. Since this is one-fourth the beat length it must be multiplied by four when substituted in equation 3 for t. The substitution, with u = 1.000294, follows:

Mean = 2.234449

$$\Delta\nu = \frac{1}{2\ ut} = \frac{1}{(2)\ (1.000294)(4 \times 2.050464)}$$

$$\Delta\nu = 0.06094389 \text{ cm}^{-1} \text{ for the } \pi/2 \text{ position.}$$

For the π position:

$$\Delta\nu = \frac{1}{2\ ut} = \frac{1}{(2)\ (1.000294)(2 \times 4.053676)}$$

$$\Delta\nu = 0.06165429 \text{ cm}^{-1} \text{ for the } \pi \text{ position.}$$

For the determination of the final value of $\Delta\nu$, the two readings were averaged. The $\pi/2$ position was given a weighting of 7/10 and the π position a weighting of 3/10. The $\pi/2$ position was given the heavier weighting since in that position the "smeared" position could be best determined. The fringes there did not completely disappear in the central portion of the field of view; thus this maximum could be more accurately located. This in turn permitted use of the filter, further rendering the $\pi/2$ position more accurate. Weighting these values of $\Delta\nu$ in this manner, the final value was taken to be

$$\Delta\nu = 0.0611570 1 cm^{-1}.$$

PART II

THEORETICAL DETERMINATION OF HYPERFINE STRUCTURE IN THE SODIUM LINES

The sodium atom in its normal state has an electron configuration of $1s^2 2s^2 2p^6 3s$ and its normal state is $^2S_{\frac{1}{2}}$. Here the K and L shells are filled. The M shell has only one electron and that is in the 3s subshell and is the 3s electron represented above. When one quantum of energy is absorbed by this 3s valence electron it goes to the next higher energy level, namely the 3p subshell. As the electron returns to the 3s state from the 3p state, it emits the radiant energy which gives us the well known D lines.

In the 3s state the azimuthal quantum number, l, of the electron is zero, since the electron is in the 3s subshell. The spin quantum number s of the electron has the value 1/2. The resultant of the orbital moment l and the spin moment s is the quantum vector j, the total angular momentum of the electron. j has the value 1/2 for the 3s electron. With the electron in the 3p state, l= 1 and s= 1/2. Consequently j has the values 1/2 and 3/2. The spectral lines emitted when the electron returns to the 3s level from the 3p level are lines of the principal series of sodium. The allowable transitions ($j=0,\pm 1$) are $3\,^2P_{1/2}-3\,^2S_{1/2}$ and $3\,^2P_{3/2}$ to $3\,^2S_{1/2}$. The first transition gives rise to the D1 line, the second to the D2 line. The above discussion is concerned only with fine structure and gives no hint of the existence of hyperfine structure.

For hyperfine structure, however, the mechanical moment of the nucleus must be taken into account. It is represented by the quantum number I. I=3/2 for sodium. Coupling the quantum vector J*, the total mechanical moment of the extranuclear electron, with the quantum vector I*, representing the total mechanical moment of the nucleus, there results a quantum vector F*. It is this resultant F* that now represents $F^*h/2\pi$, the total mechanical moment of the atom, in place of J* as previously stated for fine structure. Just as in fine structure the starred quantities are given by

$$J^* = \sqrt{J(J+1)}, \qquad I^* = \sqrt{I(I+1)}\ , \qquad F^* = \sqrt{F(F+1)} \tag{1}$$

With a nuclear spin I=3/2[1] and a J value of 1/2, the 3s state is split into two levels F=1 and 2. Again with I=3/2 and J=1/2, F has values 1 and 2 in the 3p state. For J=3/2 in the 3p state, F has the values 0,1,2, and 3. Now the selection rules for F in hfs are just the same as those for J in fine structure, viz.,

$$F=0,\pm 1 \tag{2}$$

With the new quantum number F given by a small subscript to the left of the L term type, the allowable transitions are:

(1) 3 ${}^2_3P_{3/2}$, 3 ${}^2_2P_{3/2}$ and 3 ${}^2_1P_{3/2}$ ----to---- 3 ${}^2_2S_{1/2}$

(2) 3 ${}^2_2P_{3/2}$, 3 ${}^2_1P_{3/2}$ and 3 ${}^2_0P_{3/2}$ ----to---- 3 ${}^2_1S_{1/2}$

(3) 3 ${}^2_2P_{1/2}$, and 3 ${}^2_1P_{1/2}$ ---------to---- 3 ${}^2_2S_{1/2}$

(4) 3 ${}^2_2P_{1/2}$, and 3 ${}^2_1P_{1/2}$, ---------to---- 3 ${}^2_1S_{1/2}$

The transitions (1), (2), (3), (4) give rise respectively to the

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[1] Harvey E. White, Introduction to Atomic Spectra, p. 372.

D2-1, D2-0, D1-1 and D1-0 lines mentioned in part I. It is seen that the D2-1 and D1-1 lines both terminate on the F=2 level of the 3 $^2S_{1/2}$ state. The two lines together thus have five components. Similarly, the D2-0 and D1-0 lines, terminating on the F=1 level of the 3 $^2S_{1/2}$ state, also have a total of five components. The experimental method used in part I, however is incapable of resolving these components. The separations of the D1-0 and D1-1 and of the D2-0 and D2-1 lines are the same since both terminate on the F=2 and F=1 levels. To find this separation it is necessary to compute the interaction energy between the nuclear moment I* and the electron moment J* for the states F=1 and F=2. The difference in these energies, expressed in cm^{-1}, is then the separation, in wave number units, of the two components of each of the D lines.

For a single valence electron with a specified F value, the interaction energy of this electron, screened from the nucleus by a shell of electrons, is given by[2]

$$\Gamma_F = 1/2 \; a'(F^{*2} - I^{*2} - J^{*2}) \; cm^{-1}, \qquad (3)$$

where F*, I* and J* are found from Eqs. (1). Goudsmit has suggested that we write for s electrons,[3]

$$a' = \frac{g_I}{1838} \cdot \frac{8R\alpha^2 Z_i Z_o^2}{3 n_o^3} \cdot K \; cm^{-1} \qquad (4)$$

g_I , the nuclear g factor has a value 1.4 for sodium.[4] It is the

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[2] Ibid., p. 361.

[3] Ibid., p. 363.

[4] Ibid., p. 372.

number expressing the ratio between the magnetic moment of the nucleus in nuclear magnetons ($eh/4\pi Mc$) and the mechanical moment of the nucleus in quantum units of $h/2\pi$.

R is the Rydberg constant for sodium and is given by[5]

$$R = \frac{R_\infty}{1 + \frac{m}{AM_p}} \qquad (5)$$

where R_∞ is the Rydberg constant for infinite mass; m, the mass of the electron is 1; A is the atomic weight (23) of sodium; and M_p is one-sixteenth the mass of an oxygen atom expressed in terms of the electron mass. Evaluation of R yields the value 109734.838 cm^{-1}.

The fine-structure constant α (eq. 4) equals $2\pi e^2/hc$. α^2 has the value 5.305×10^{-5}.[6]

Referring again to Eq. 4, Z_i is the effective nuclear charge inside the core of closed electron shells. For s electrons, $Z_i \cong Z$.[7] Z_o, the effective nuclear charge outside the core of closed electron shells, has the value unity for sodium.

n_o represents the effective quantum number n*. For an s electron with l=0 and the principal quantum number n=3, n_o= n*=1.627.[8]
$n_o^3 = 4.30687888$.

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[5] Ibid., p. 35.

[6] Ibid., p. 437.

[7] Ibid., p. 363.

[8] Ibid., p. 90.

The relativity correction K is given by[9]

$$K = \frac{4j(j+\frac{1}{2})(j+1)}{(4\rho^2-1)\rho}, \qquad \rho^2 = (j+\tfrac{1}{2})^2 - (\alpha Z_i)^2, \tag{6}$$

With $j=1/2$, ρ^2 is 0.993581907 and $\rho = 0.996785789$. Evaluation of K gives $K=1.01188373$.

Upon substituting these values in Eq. (4), it is found that $a'=0.03055919\ \text{cm}^{-1}$.

The interaction energy for F=2 is found from Eq. (3),

$$\Gamma_{F=2} = \frac{3}{4}a' \tag{7}$$

where $I=3/2$ and $J=1/2$.

For F=1, I and J having the above values, the interaction energy is

$$\Gamma_{F=1} = -\frac{5}{4}a' \tag{8}$$

The energy difference between the levels F=2 and F=1 is

$$\Delta\Gamma = \Gamma_{F=2} - \Gamma_{F=1} = 2a' \tag{9}$$

Consequently $\Delta\Gamma = 0.06111838\ \text{cm}^{-1}$ and this is the wave number separation between the D1-0 and D1-1 and between the D2-0 and D2-1 lines.

The theoretical result is then

$$\Delta\nu = 0.06111838\ \text{cm}^{-1} \tag{10}$$

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9 *Ibid.*, p. 362.

PART III

CORRELATION OF EXPERIMENTAL AND THEORETICAL FINDINGS

Between the experimental result $\Delta\nu=0.06115701$ cm^{-1} and the theoretical result $\Delta\nu=0.06111838$ cm^{-1} there is a difference of 0.00003863 cm^{-1}. With the theoretical result taken to be correct, this gives an error of 0.063 of one percent for the experimental result.

When the two values are averaged, each varies from the mean by 0.032 of one percent.

Thus there is excellent agreement between theory and experiment.

We know of only one case on record where hyperfine structure of sodium has been determined experimentally.[1] Here Schuler[2] discovered that each one of the yellow sodium lines is double and showed that the lowest s state of sodium possesses a hyperfine structure with $\Delta\nu=$ 0.060 cm^{-1}. A copy of his paper was not available for study but it is quite probable that his result was found by measurements of the radii of the ring systems photographed when sodium light from a source slit was dispersed by a prism after passing through the Fabry-Perot etalon. The prism here is placed between the half-silvered plates and the converging lens. An excellent description of this method is given by Williams.[3]

The results recorded in this paper are of the same magnitude as

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[1] L. Pauling and S. Goudsmit, Structure of Line Spectra, p. 224.

[2] H. Schuler, Naturwiss., 16; 512, 1928.

[3] W. E. Williams, Applications of Interferometry, pp. 83-88.

that of Schuler. Scale readings in part I are accurate to six decimal places. Hence the experimental value of $\Delta\nu$ is accurate to six significant figures. In our opinion the theoretical value of $\Delta\nu$ is also accurate to at least six figures.

It is, therefore, our conclusion that the sodium D lines are split due to a nuclear interaction, the separation being approximately equal to $0.06113769\ cm^{-1}$.

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