The Nuclear Moments of Columbium from Hyperfine Structure

STANLEY S. BALLARD, *Department of Physics, University of California, Berkeley*

(Received September 18, 1934)

The hyperfine structure of the arc spectrum of columbium has been examined under conditions of high resolving power. The line patterns of λλ4059, 4080, 4117, 4137, 4168, 4649, 4672, 4675, 5344 and 6661 have been studied in detail. Three relatively independent methods have been used to determine the nuclear mechanical moment, $I^*h/2\pi$. All three methods indicate a value of 9/2 for I, the quantum number of nuclear spin. Using the formulas given by Goudsmit, the nuclear g-factor has been calculated to be $g_I=0.83$. This gives for the nuclear magnetic moment $\mu_I=3.7$ nuclear magnetons.

INTRODUCTION

MANY lines in the spectra of neutral and ionized columbium ($Z=41$, $M=93$) were found by King[1] to show wide hyperfine structure splittings. The spectrum of the neutral atom was photographed under higher resolution by Dr. N. S. Grace. After a qualitative examination of these plates Grace and the author gave the preliminary result[2] that $I\geq 7/2$ for columbium. The present investigation was undertaken for the purpose of fixing the value of I definitely, and if possible, evaluating also μ_I.

In an investigation of this kind one ordinarily examines only classified lines. Although the spectrum of Cb I is unfortunately only partially analyzed, the classifications of a number of lines lying between λ3500 and λ4218 have been given by Meggers and Kiess.[3] They grouped these lines into five multiplets with the common lower level $4d^45s\ {}^6D$. The upper levels given were ${}^6F^\circ$, ${}^6P^\circ$, ${}^6D^\circ$, ${}^6D'^\circ$, ${}^6P'^\circ$, the first three of these being attributed[4] to a $4d^45p$ configuration. Unfortunately these lines lie in a region of low resolving power of the Fabry-Perot etalons used (due to the low reflecting power in the violet of the silver with which the etalon plates were coated[5]). Hence it was deemed necessary to examine unclassified lines also.

APPARATUS AND EXPERIMENTAL PROCEDURE

The columbium spectrum was produced in the electrical discharge in an argon-filled Schüler tube into the cathode base of which a hollow cylindrical shell of columbium metal had been forced. The tube operated on 2000 volts d.c. with currents ranging from 0.06 to 0.30 amp. In order to cut down the Doppler broadening of the radiated lines the tube was partially immersed in liquid air during operation. The high resolving power necessary was obtained through the use of a Fabry-Perot etalon. The distance between the etalon plates was regulated by invar ring separators, the separators used varying in width from 2.5 mm to 15 mm. A three prism glass spectrograph of one meter focus was used to produce the necessary auxiliary dispersion. The spectrum was photographed in exposure times of from five minutes to two hours. In order to photograph λ6661 it was found necessary to use ammonia-sensitized Hypersensitive Panchromatic plates. For λ5344 Panchromatic plates were used, and for all other lines the finer-grained "33" plates were used. The plates to be used in intensity work were developed in rodinal, 1 : 20. These plates were calibrated for intensity measurements by use of a step-slit as described by Anderson.[6] The intervals between hfs. components were measured with a comparator on densitometer records made from the original plate by a Zeiss recording microphotometer. The relative peak intensities of the hfs. components of a line pattern were reduced from the densitometer records as described by Anderson.[6]

[1] A. S. King, Astrophys. J. **73**, 13 (1931).
[2] N. S. Grace and S. S. Ballard, Phys. Rev. **44**, 128A (1933).
[3] W. F. Meggers, J. Wash. Acad. Sci. **14**, 442 (1924); W. F. Meggers and C. C. Kiess, J. Opt. Soc. Am. **12**, 417 (1926).
[4] R. F. Bacher and S. Goudsmit, *Atomic Energy States*, p. 124 (McGraw-Hill, 1932).
[5] H. E. White and S. S. Ballard, Phys. Rev. **39**, 545A (1932).
[6] O. E. Anderson, Phys. Rev. **45**, 685 (1934).

Experimental Results

A survey of the visible spectrum of Cb I photographed under high resolution suggested that the hyperfine structure of the line patterns is to be attributed to the coupling of a magnetic nucleus with the valence electrons, rather than to the so-called isotope effect. By no means *all* of the spectrum lines show hfs. splittings, however. The group of classified lines lying between λ4059 and λ4218 (the only classified lines in the visible region) show a wide hfs. degrading toward the violet. This indicates that the lower level arises from a configuration containing a tightly-bound, deeply-penetrating *s* electron. This is indeed the case, as these lines represent the transitions $4d^45s\ {}^6D-4d^45p\ {}^6F^\circ$, ${}^6P^\circ$. A group of unclassified lines in the blue show a wide hfs. degrading, in general, toward the red. λ4672 and λ4675 are the most prominent of these. A comparison with the analyzed terms of vanadium (the spectroscopic homologue of columbium) suggests that these lines may be some of the transitions $4d^35s^2\ {}^4F$, ${}^4P-4d^35s5p\ {}^6G^\circ$, ${}^6D^\circ$, ${}^6F^\circ$, ${}^4G^\circ$, etc. Since the penetrating *s* electron is in this case in the *upper* configuration the patterns would be expected to degrade toward the *red* as observed rather than toward the violet, as in the former group of lines. Other scattered lines show wide hfs., the most prominent being λ5344 in the green and λ6661 in the red. The overall widths of the most prominent lines are as follows: the violet line λ4059, $\Delta\lambda=0.15$A, $\Delta\nu=0.93$ cm^{-1}; the blue line λ4672, $\Delta\lambda=0.21$A; the green line λ5344, $\Delta\lambda=0.17$A; the red line λ6661, $\Delta\lambda=0.63$A, $\Delta\nu=1.42$ cm^{-1}.

A. The evaluation of I

The mechanical moment of an atomic nucleus is given by $I^*h/2\pi$, where $I^*=[I(I+1)]^{\frac{1}{2}}$. What one evaluates experimentally is I, the quantum number of nuclear spin. Three essentially different methods were used in evaluating I for columbium. The first of these consisted simply in counting the number of diagonal components in a so-called "flag type" hfs. line pattern. In the case of lines for which J of the widely split level $\geq I$ there should be $2I+1$ of these diagonal components. The pattern of λ5344 (see Fig. 1), for example, shows six components degrading uniformly in intensity and interval. Hence either $J\geq 5/2$ or $I\geq 5/2$ (or both) for the more widely split level involved. On one very good plate λ4672 shows eight evenly degrading components and in addition an unresolved tail possibly large enough to contain at least two more components. This shows that $I\geq 7/2$ and may be as large as 9/2. It was upon such evidence that the preliminary estimate[2] of the magnitude of I for columbium was based.

The second method consisted in measuring the peak intensities of the components of an hfs. line pattern and comparing them with the values calculated for various values of I. Although this process was carried through for several lines[7] only the two most trustworthy determinations will be mentioned here. The first line examined, λ4117, represents the transition $4d^45s\ {}^6D_{1/2}-4d^45p\ {}^6P_{3/2}^\circ$. It appears as a well-defined doublet with a separation of 0.29 cm^{-1} between components. If this splitting is attributed to the lower (${}^6D_{1/2}$) level, an examination of the densitometer trace of the line pattern shows that the upper level is quite sharp; $\Delta\nu\leqq 0.01$ cm^{-1}. Hence the theoretical relative intensities of the two components of the hfs. doublet should be given by the summation rule of intensities as applied to the two hfs. levels of ${}^6D_{1/2}$. Table I shows the relative inten-

[7] S. S. Ballard, Phys. Rev. **46**, 327A (1934).

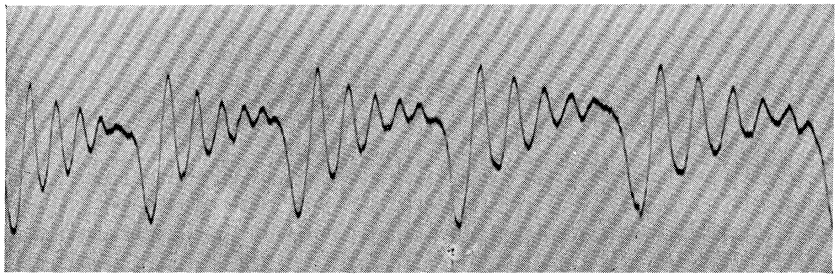

Fig. 1. Reproduction of a portion of a densitometer trace of Cb λ5344 (6.5 mm etalon separator).

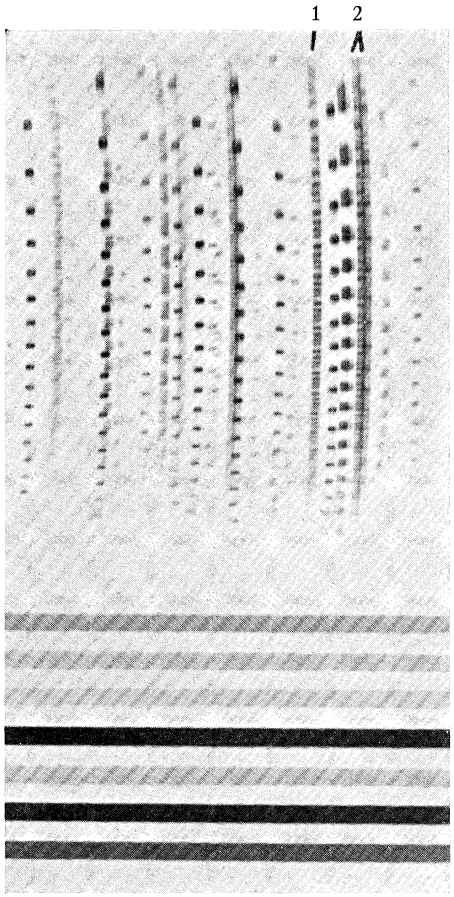

FIG. 2. Reproduction of portion of plate showing Cb hfs. (9 mm separator). λ4649 is marked "1"; λλ4672 and 4675 (overlapped with this separator) are marked "2." The plate carries intensity calibration marks put on with a seven aperture step-slit.

sities computed for $I=7/2$, 9/2, and 11/2 together with the observed relative intensities (an average of several determinations).

TABLE I. *Calculated relative intensities for a level with $J=1/2$, and observed values for λ4117.*

Calculated			Observed
$I=7/2$	9/2	11/2	λ4117
1.29	1.22	1.18	1.23

The second line examined, λ4649, is a prominent unclassified line whose hfs. pattern consists of four sharp components degrading regularly in interval and intensity toward the violet. This indicates that one level is quite sharp, and that for the widely split level $J=3/2$. Fig. 2 shows a portion of the visible spectrum of columbium as photographed under high resolution. The four component line λ4649 is marked "1." Fig. 3 shows an enlargement of the line pattern and the corresponding densitometer trace. In Fig. 4 the experimental intensity data obtained from this line are shown graphically. It shows the peak intensities (in arbitrary units) of the four components plotted against the order of interference (numbered arbitrarily) for nine orders. The sloping off of all four curves indicates that there is a variation of intensity with order and also that there may have been a variation of the intensity of the light source along the length of the slit. However since the curves are quite parallel these factors will not influence the *relative* intensity values obtained for the four components. Experimental intensity values were taken from these curves at four ordinates and the values for each component were averaged. These were reduced to a convenient arbitrary scale by assigning to the strongest component an intensity of 100. These reduced average experimental values are shown in Table II, together with the

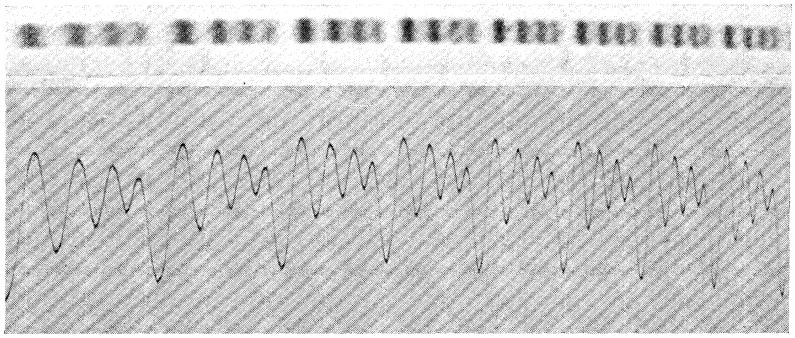

FIG. 3. Reproduction of Fabry-Perot etalon pattern and corresponding densitometer trace of Cb λ4649 (9 mm separator).

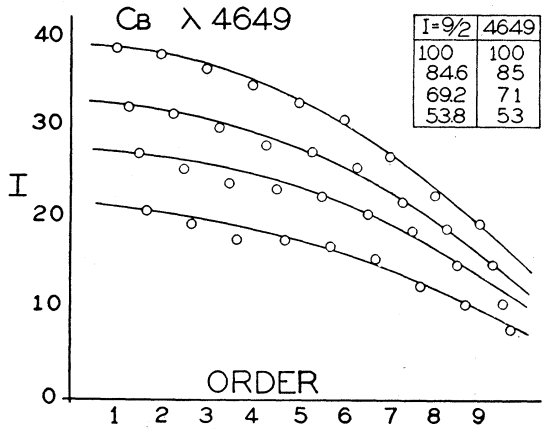

FIG. 4. Peak intensity I (in arbitrary units) of the four components of λ4649 plotted against order of interference (numbered arbitrarily). Table shows agreement of average reduced observed relative intensities with values calculated for $I=9/2$, $J=3/2$.

TABLE II. *Calculated relative intensities for a level with $J=3/2$, and observed values for λ4649.*

$I=7/2$	Calculated 9/2	11/2	Observed λ4649
100	100	100	100
81.8	84.6	86.7	85
63.6	69.2	73.3	71
45.4	53.8	60.0	53

theoretical values for $I=7/2$, $9/2$ and $11/2$ calculated by use of the summation rule as applied to a level with $J=3/2$. The observed values again check closely the calculated values for $I=9/2$.

The third method used in evaluating I was the comparison of observed intervals between hfs. components with theoretical intervals calculated from the Landé interval rule as applied to hyperfine structure. The observed intervals for several of the lines which were measured are listed in Table III. The overall width of each line is given since in most cases complete resolution of the line pattern was not effected. λ4117, as mentioned above, has a doublet separation of 0.29 cm^{-1} which was attributed chiefly to the splitting of the $^6D_{1/2}$ level. Measurements on λ4168 ($^6D_{1/2}-{}^6F_{1/2}°$) gave the intervals $\Delta\nu=0.30$ cm^{-1} for $^6D_{1/2}$ and $\Delta\nu=0.25$ cm^{-1} for $^6F_{1/2}°$. All observed intervals listed represent the average values obtained by measuring from six to ten orders on each plate. Since the dispersion along the interference pattern is not linear these average values were obtained by the use of Newton's interpolation formula for *divided differences*. The second divided differences were found to be random, as was expected since the dispersion follows the parabolic law $d\lambda/dx=-kx$, where x is the distance from the center of the etalon pattern.

In order to facilitate the comparison of these observed intervals with calculated values all intervals are reduced to a common arbitrary scale by assigning to the first interval of each line pattern the magnitude 100. Table IV shows the calculated and observed interval ratios for λ4059, $4d^45s\ ^6D_{9/2}-4d^45p\ ^6F_{11/2}°$. This is the first ultimate line of columbium as assigned by de Gramont, and is the widest line in the violet. The greater splitting has been attributed to the lower level since it arises from a configuration containing a tightly-bound s electron. Hence the theoretical ratios given in Table IV are those

TABLE III. *Observed hfs. intervals in cm^{-1} for various line patterns.*

	λ4059	λ4080	λ4649	λ4672	λ4675	λ5344	λ6661
1st	0.190	0.148	0.151	0.168	0.110	0.152	0.305
2nd	0.168	0.130	0.126	0.152	0.098	0.130	0.262
3rd			0.099	0.136	0.086	0.115	0.233
4th			——	0.120	0.070	0.093	
5th				0.106			
overall	0.932	0.630	0.376	0.943	0.542	0.607	1.416

TABLE IV. *Calculated and observed interval ratios for λ4059.*

	Calculated ratios for $J=9/2$ $I=7/2$	8/2	9/2	10/2	11/2	Observed ratios for λ4059
	100	100	100	100	100	100
	87.5	88.2	88.9	89.5	90.0	88
	.	.	.	.	.	.
	.	.	.	.	.	.
	.	.	.	.	.	.
overall	437.5	476.4	500.0	526.3	540.0	491

calculated for a fine structure term with $J=9/2$. Only the first two intervals and the overall width of this line pattern could be measured with accuracy due to the poor resolving power of the etalons in the violet. However, there is good agreement with the calculated values for $I=9/2$.

λ4080, the second ultimate line, represents the transition $4d^45s\ ^6D_{7/2}-4d^45p\ ^6F_{9/2}°$. The observed ratios in Table V are hence shown as com-

TABLE V. *Calculated and observed interval ratios for λ4080.*

	Calculated ratios for $J=7/2$			Observed ratios
	$I=7/2$	9/2	11/2	for λ4080
	100	100	100	100
	85.7	87.5	88.9	88
	.	.	.	.
	.	.	.	.
	.	.	.	.
	.....	.....	.....	.....
overall	400.0	437.5	466.7	426

pared to those calculated for a level with $J=7/2$. Again only two intervals could be measured with accuracy.

λ4649 is the unclassified four-component line shown in Figs. 2 and 3. The calculated interval ratios given in Table VI are for a fine-structure

TABLE VI. *Calculated and observed interval ratios for λ4649*

Calculated ratios for $J=3/2$			Observed ratios
$I=8/2$	9/2	10/2	for λ4649
100	100	100	100
81.8	83.3	84.6	83.4±0.1
63.6	66.7	69.2	65.6±0.1

level with $J=3/2$. The observed ratios given are the average values for ten orders, the proportional errors indicated being those involved in obtaining the arithmetic means for the ten orders. The observed ratios check the calculated values for $I=9/2$ very closely. The reason that the third observed interval is small is probably that the fourth component, being close to the third component and weaker than it, is pulled in slightly toward it (cf. Fig. 3). Although a half-integral value of I would be predicted for columbium since it has odd atomic weight, it is to be emphasized that the interval measurements of λ4059 and λ4649 distinguish clearly between 8/2, 9/2 and 10/2 as possible values of I.

In the case of an element for which the value of I is known the observed hfs. intervals of a line pattern can often be used to determine the J-value of the more widely split level involved. This was done for four unclassified lines whose interval measurements are given in Table III. Accepting the value $I=9/2$ for columbium, theoretical interval ratios were computed from the Landé interval rule for various values of J. A comparison of observed interval ratios with these calculated ratios showed immediately what J-value to assign to the more widely split level associated with each line. Whether this was the upper or lower level was decided by seeing whether the line pattern degraded toward the red or the violet. The results for the four lines are as follows: (a) λ4672; $J=11/2$ (possibly 13/2) for the upper level, (b) λ4675; $J=9/2$ for the upper level, (c) λ5344; (see Fig. 1) $J=5/2$ for the upper level, (d) λ6661; $J=7/2$ for the upper level. Data such as these should be of use in analyzing the multiplet structure of a spectrum when Zeeman effect patterns are not available.

B. The evaluation of μ_I

The nuclear g-factor g_I and the nuclear magnetic moment μ_I of columbium have been calculated following the method suggested by Goudsmit.[8] The coupling factor a of the $5s$ electron was computed from the Bacher-Goudsmit[9] equation to be 0.13 cm^{-1}, using the measured splitting 0.30 cm^{-1} of the $4d^4(^5D)5s\ ^6D_{1/2}$ level. This value, substituted in Goudsmit's formula[8] for an s electron, gave $g_I=0.83$. Since $I=9/2$ for columbium the value of the nuclear magnetic moment is approximately $\mu_I=3.7$ nuclear magnetons. (One nuclear magneton $=eh/4\pi Mc$, where M = the mass of the proton.) It is of interest that these values of I, g_I, and μ_I are practically identical with those[8] of Bi^{209}. The value of μ_I for columbium must however be regarded as accurate only as to order of magnitude. The reasons for this are the following:

(a) The ionization potential of $_{41}$Cb is as yet unknown, and its value (which is needed in the formula for g_I) was therefore interpolated linearly between the known values of $_{40}$Zr and $_{42}$Mo.

(b) The value of a for the $5s$ electron was obtained from only one term, $^6D_{1/2}$. It would be preferable to have several different determinations of its magnitude.

(c) The formulas of Goudsmit[8] are claimed to give only "fair approximations for the nuclear magnetic moment."

[8] S. Goudsmit, Phys. Rev. **43**, 636 (1933).
[9] L. Pauling and S. Goudsmit, *The Structure of Line Spectra*, p. 209 (McGraw-Hill, 1930).

Conclusions

The results of this investigation may be summarized[10] as follows:

(1) The observed hyperfine structure in the arc spectrum of columbium can be accounted for by attributing mechanical and magnetic moments to the columbium nucleus.

(2) The quantum number of nuclear spin of columbium is given by $I=9/2$.

(3) Approximate values of the nuclear g-factor and nuclear magnetic moment of columbium are $g_I=0.83$, $\mu_I=3.7$ nuclear magnetons.

In conclusion the writer wishes to express his sincere thanks to Professor H. E. White, who has guided him throughout this investigation. He also wishes to acknowledge the help of Professor F. A. Jenkins in interpreting intensity data, and the cooperation of Doctor N. S. Grace, with whom the work was first undertaken.

[10] See also S. S. Ballard, Phys. Rev. **46**, 233L (1934).

NOVEMBER 1, 1934 PHYSICAL REVIEW VOLUME 46

An Experimental Determination of Ultrasonic Absorption and Reflection Coefficients in Air and in Carbon Dioxide

Roger W. Curtis, *Department of Physics, The Johns Hopkins University*

(Received September 4, 1934)

Ultrasonic absorption coefficients in air and in carbon dioxide have been measured, as well as the coefficients of reflection in these gases at a solid boundary. In the frequency range between 88 and 1000 kc/sec. the absorption in air was found to increase with the square of the wave-length as required by classical theory, but for CO_2 the absorption constant of the classical theory rises to a sharp maximum at about 98 kc/sec. The reflection coefficient (brass reflector) was found to decrease with increasing frequency for both gases, the decrease being of the order of twenty percent at the higher frequencies. Measurements on an impure sample of helium are included.

THE method developed by Hubbard[1] for determining ultrasonic absorption and reflection coefficients by means of the acoustic resonator interferometer has been used in this investigation. The source of ultrasonic waves was in each case a vibrating piezoelectric quartz plate, which acted as a source of plane waves, the wave-length of which was small compared to the diameter of the source. The quartz plate was not self-oscillating but was forced to vibrate at one of its natural resonance frequencies by an external source of periodic electromotive force applied to the plate. This plate closed one end of a tube and thus radiated ultrasonic waves into it. The other end of the tube was closed by a piston, the position of which could be changed by a micrometer screw. The reaction of the vibrating column of gas in the tube upon the quartz plate, as in all work with the acoustic interferometer, varies cyclically with the position of the piston, reaching maximum values as the piston passes through resonance positions, in which standing waves are set up. Hubbard has shown that the gas column and crystal may be regarded as a single mechanical system, the impedance of which varies periodically with reflector distance. These variations can be measured quantitatively and from them can be calculated the coefficient of absorption in the gas as well as the reflection coefficient at the surface of the piston. If no energy were absorbed then the reaction of the gas column on the quartz plate would be the same for all sets of standing waves produced as the piston moves away from it. Since, however, energy is absorbed in the gas the resonance reaction diminishes as the piston recedes from the source until, at sufficiently great distances, there should be no reaction and hence no system of standing waves. The experimental work consists, in a given case, in measuring the reaction for a series of reflector distances. From these readings the coefficients of absorption and reflection are evaluated.

[1] J. C. Hubbard, Phys. Rev. **38**, 1011 (1931); **41**, 523 (1932).

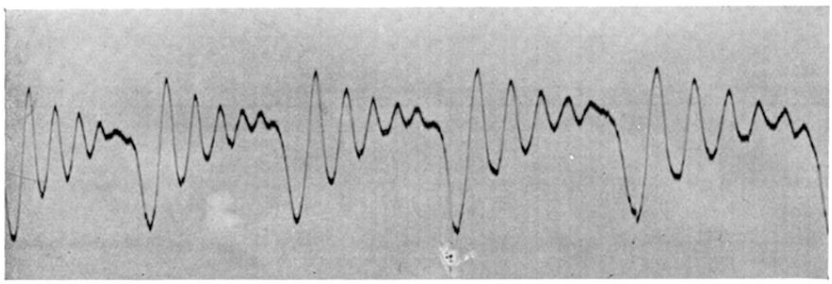

FIG. 1. Reproduction of a portion of a densitometer trace of Cb λ5344 (6.5 mm etalon separator).

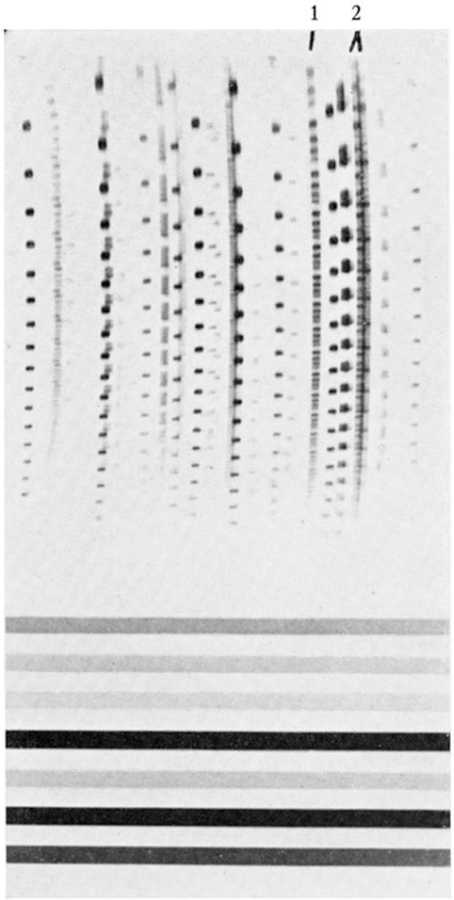

FIG. 2. Reproduction of portion of plate showing Cb hfs. (9 mm separator). λ4649 is marked "1"; λλ4672 and 4675 (overlapped with this separator) are marked "2." The plate carries intensity calibration marks put on with a seven aperture step-slit.

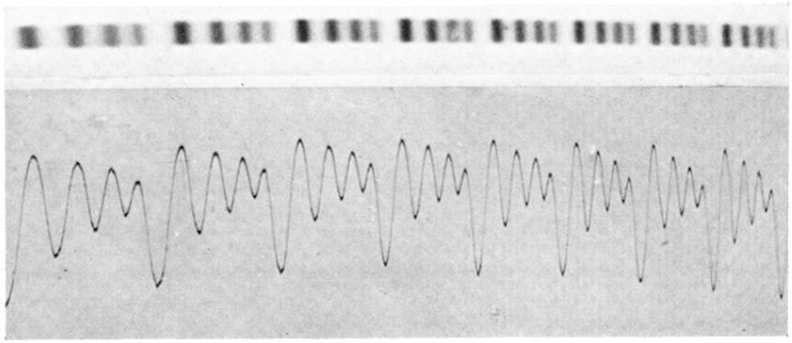

FIG. 3. Reproduction of Fabry-Perot etalon pattern and corresponding densitometer trace of Cb λ4649 (9 mm separator).