The Hyperfine Structure of Cs II

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The first spark spectrum of caesium was photographed in the visible region with equipment including an electrodeless discharge, a Fabry-Perot interferometer, and a glass Littrow-type spectrograph. The hyperfine structure of thirteen lines was measured and twelve of the patterns were analyzed and identified as being caused by transitions between the $5p^5(^2P_{\frac{1}{2}})6p$ terms and the $5p^5(^2P_{\frac{1}{2}})5d$, $6s$, $6d$, $7s$, and $5p^5(^2P_{1\frac{1}{2}})7d$, $8s$ terms of the energy level scheme established by Sawyer, Olthoff, and others. This analysis verified the J values of seven levels given by Olthoff and Sawyer, determined the interval factors for nine energy levels, established one new energy level, and fixed the J value for one of the levels suggested by Ricard. A tentative identification of the two terms with the largest interval factor as $5p^5(^2P_{\frac{1}{2}})6s\,^1P_1$ and $5p^5(^2P_{\frac{1}{2}})7s\,^1P_1$ leads to 202,263 cm^{-1} as an approximate value of $5p^6\,^1S_0$.

INTRODUCTION

THE first accurate measurements of the h.f.s. in Cs II were made by Kopferman[1] on nine lines that involved transitions from four $5p^56p$ levels to four $5p^55d$, $6s$ levels. The results of Kopferman's experiment indicated that for caesium the nuclear moment is 7/2, and established interval factors and J values for the eight levels.

The present work was undertaken with a view to distinguishing the s levels from the d levels, to establishing more definitely the J values of known energy levels, and to locating undiscovered energy levels.

EXPERIMENTAL PROCEDURE

In this research, as in the work described in the preceding paper, an electrodeless discharge was used as a source. The discharge tube, 10 inches long and about 1 inch in diameter, wound with 20 turns of woven-wire braid, was placed in an electrically heated transite box and arranged for end-on observation. The exciting current was provided by a Tesla discharge. The discharge in the tube was started at a temperature of approximately 180°C and continued intermittently for 25 seconds in each minute; longer operating periods caused excessive heating of the quartz tube.

To minimize relative vibrations, the Fabry-Perot interferometer and the Hilger El glass spectrograph were supported by a heavy cast-iron frame work. To reduce temperature and pressure fluctuations, the interferometer, equipped with invar separators, a 50-cm focal length collimating lens, and a 60-cm focal length achromatic converging lens, was enclosed in an airtight box. The temperature of the air in this compartment was kept constant to within two tenths of a centigrade degree. As is well known, the fringe shift owing to change of temperature is negligible, provided the separators are made of invar. Variations in pressure, however, produce serious fringe shifts and therefore must be avoided.

The quartz interferometer plates, 6 cm in diameter, were supported in a cylindrical frame so designed that pressure could be applied to the plates at three symmetrically located points by three independent T-shaped springs. The plates were silvered by an evaporation method in a chamber large enough to allow a maximum distance of 15 cm from the filament to each mirror. For the most part, a point source was

TABLE I. Lines and h.f.s. intervals.

λ(air)	h.f.s. intervals (cm^{-1})				
4158.610	0.531	0.440	0.389	0.284	
4616.13	0.758	0.586			
4623.091	0.589	0.457	0.152		
4656.538	0.606	0.471			
4763.616	0.225	0.174			
4870.024	0.288	0.370	0.376	0.302	
4879.95	0.211	0.540	0.405	0.412	0.143
5059.866	0.146	0.203	0.265	0.316	
5081.773	0.171	0.228			
5209.58	0.473	0.612			
5349.16	0.275	0.333	0.240	0.497	
5358.53	0.497	0.657			
5579.033	0.447	0.590			

[1] H. Kopferman, Zeits. f. Physik **73**, 437 (1931).

used for the evaporation of the silver but in a few cases a symmetrically located ring filament was used to greater advantage.

The caesium discharge was photographed throughout the visible region with intermittent exposure times equivalent to as much as two hours and with interferometer separators of 2, 3, 5, 7.5, and 10 mm. Eastman spectroscopic plates N, F, and O of types II, III, 144, and IV were used and were developed in Eastman D19

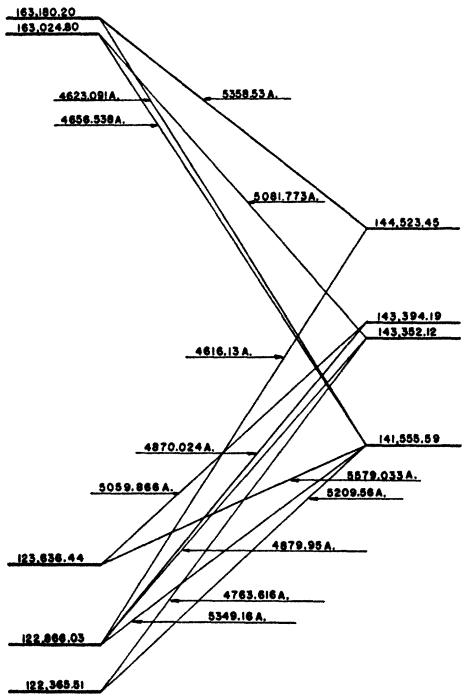

FIG. 1. Partial energy level diagram of Cs II.

developer. It was found expedient when using N and F plates in the 6000A region to hypersensitize them with ammonium hydroxide.

RESULTS

In Table I are listed the lines and the hyperfine structure intervals as measured in this research. The h.f.s. intervals are tabulated so that the wave-length decreases from left to right. Figure 1 is a partial energy-level diagram showing how these lines fit into the energy-level scheme of the preceding paper. The term values as given are based on the $5p^6\ {}^1S_0$ level.

All the lines analyzed will be seen to involve transitions with the four $5p^5(^2P_{\frac{1}{2}})6p$ terms found by Olthoff and Sawyer.[2] The reality of these $6p$ terms and the correctness of the assigned J values are definitely established by the results. The hyperfine structure of the combinations of all four of these terms with the term ν122,866 has been measured, as well as that of two of them to the term ν122,365. These terms, both classified as $J=1$ terms in the group $5p^5(^2P_{\frac{1}{2}})5d$, $6s$, are thereby corroborated. So also is the term ν163,180, in the $5p^5(^2P_{\frac{1}{2}})7d$, $8s$—$5p^5(^2P_{\frac{1}{2}})6d$, $7s$ group, for which two transitions to the $(^2P_{\frac{1}{2}})6p$ group have been analyzed. From these six lines the interval factors of the four $(^2P_{\frac{1}{2}})6p$ terms have been determined, as given in Table II.

The intervals and separations measured for the lines, 5209A and 4656A, indicate that these lines are combinations of levels having $J=0$ with the level, ν141,555. In the same way, the lines 5081A and 4763A are also seen to be combinations of the level, ν143,352, with two levels with $J=0$, and, in fact, with the same two levels as in the preceding case.

Of the two levels thus confirmed, the higher, ν163,024 was first given by Ricard.[3] This level and ν197,642, included in the preceding paper, are the only two of the nineteen levels suggested by Ricard and his associates that have been confirmed in the present researches. Ricard suggested for this level the configuration $5p^46s6p$. It falls, however, among the levels assigned in the previous work in this laboratory to the configurations $5p^5(^2P_{1\frac{1}{2}})7d$, $8s$ and $5p^5(^2P_{\frac{1}{2}})6d$, $7s$ and has been so included in the classification by Wheatley and Sawyer.

TABLE II. Interval factors.

Level	J value	Interval Factor
141,555.59	1	0.137
143,352.12	1	−0.049
143,394.19	2	0.064
144,523.45	0	0
122,866.03	1	0.168
123,636.44	1	0.0117
163,024.80	0	0
163,180.20	1	0.144
122,365.51	0	0

[2] J. Olthoff and R. A. Sawyer, Phys. Rev. **42**, 6 (1932).
[3] R. Ricard, Comptes rendus **206**, 905 (1938); R. Ricard, M. Givoid, and F. George, Comptes rendus **205**, 1229 (1937).

The other $J=0$ level, $\nu 122{,}365$ is new. It falls in the group of $5p^5(^2P_{\frac{1}{2}})5d$, $6s$ levels, and has displaced in this group the former $J=0$ level, which was less well established. Wheatley and Sawyer found two additional combinations of this level with the levels of the $7p$ group which give it additional support.

Six of the lines measured are clearly transitions between levels having J values of 0 and 1; three being from $J=0$ to $J=1$, and three from $J=1$ to $J=0$. In these cases, since the nuclear moment is known to be 7/2, the $J=0$ level has one hyperfine level for which $F=7/2$, and the $J=1$ level has three, for which $F=9/2$, 7/2, and 5/2, by virtue of the rule that F can take on values of $J+I$, $J+I-1$, $\cdots$ $J-1$. The hyperfine structure pattern of such a transition accordingly has three components which, following the interval rule, should have spacings of $9/2\ A$ and $7/2\ A$, where A is the interval factor for the $J=1$ level, and should have intensities in the ratio 5 : 4 : 3.

These conditions were very well satisfied by the patterns obtained for the above-mentioned lines. In the case of lines 4616A and 4763A where the measurements were made on patterns from interferometer separators of three different values, 2, 3, and 5 mm for line 4616A, and 3, 5, and 7.5 mm for line 4763A—the ratio of the large interval to the small interval did not differ from the theoretical ratio of 9/7 by more than $1\frac{1}{2}$ percent.

The analysis of the remaining six lines, indicated in Fig. 1, which involve levels with J values other than zero, was aided by the use of Fisher-Goudsmit[4] analysis diagrams. Figure 2 is the analysis diagram for a transition between levels with $J=1$. In the use of this diagram to interpret h.f.s. patterns, if both terms have normal h.f.s. and obey the interval rule, there are three F levels of 9/2, 7/2, and 5/2 in each term separated by distances of $9/2\ A$ and $7/2\ A$ in the upper term and by distances of $9/2\ B$ and $7/2\ B$ in the lower term, where A and B are the interval factors for the upper and lower terms, respectively. Upon application of the selection rules, i.e., $\Delta F=\pm 1$, 0 (0→0 excluded) and use of $Y=A/B$, the displacements of the lines from the line representing the transition 7/2 to 7/2 are,

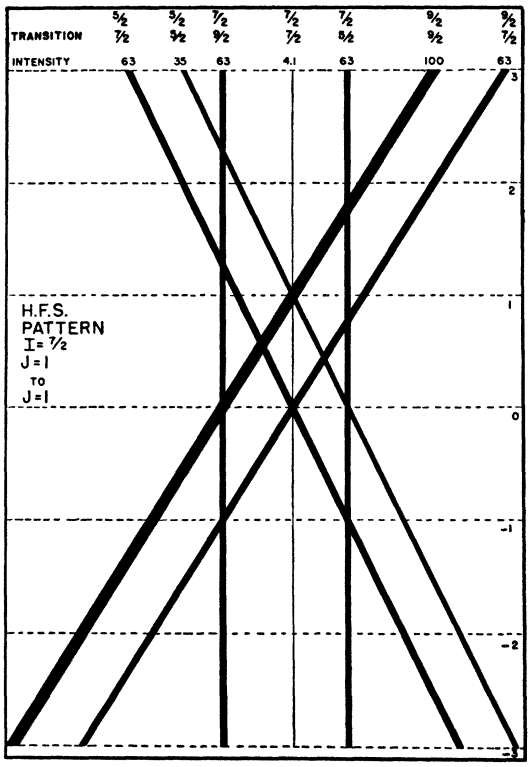

FIG. 2. Fisher-Goudsmit diagram for analysis of h.f.s. The case shown is that for a transition between two terms with $J=1$ when $I=7/2$.

$-9/2\ B$ for 7/2 to 9/2, $+7/2\ B$ for 7/2 to 5/2, $+9/2\ B(Y-1)$ for 9/2 to 9/2, $+9/2\ BY$ for 9/2 to 7/2, $-7/2\ BY$ for 5/2 to 7/2, and $-7/2\ B(Y-1)$ for 5/2 to 5/2. If one of the two terms is inverted, i.e., the largest F value lying deepest, Y has a negative value. When the displacements are plotted against positive and negative values of Y a straight line results for each transition. The relative intensities of these lines, as given by the intensity rules of Hill,[5] are written above the transition values and are also approximately represented by the width of the straight lines.

In the case of the line 5349A, the pattern has five components, with estimated intensities of 2, 2, 4, 1, and 6, and separations of 0.275, 0.333, 0.240, and 0.497 cm^{-1}, respectively. This transition if correctly assigned involves two of the $J=1$ levels for which the interval factors have been evaluated from their combinations with $J=0$ levels. The h.f.s. pattern should then be

[4] R. A. Fisher and S. A. Goudsmit, Phys. Rev. **37**, 1057 (1931).

[5] E. L. Hill, Proc. Nat. Acad. Sci. **16**, 68 (1930).

found on Fig. 2 and the spacings in the pattern can be calculated with the aid of the interval rule and the known interval factors. The pattern is found on Fig. 2 at $Y \leqq 0.8$ and it is seen that it is completely resolved except for the 7/2 to 5/2 and 9/2 to 7/2 components, which very nearly have the same displacement. The component due to the 7/2 to 7/2 transition is not observed because of its extremely low intensity. The interval 0.275 cm represents the difference between the transition 7/2 to 9/2 and the transition 5/2 to 7/2 and, therefore, according to the interval rule, is equal to $4/5 \times 0.168 - 3.5 \times 0.137$, where 0.168 cm^{-1} and 0.137 cm^{-1} are the interval factors previously determined for the lower and upper energy levels, respectively. The calculated value of the interval, 0.2765 cm^{-1} is in very good agreement with the observed value. The second interval in the observed pattern of 0.333 cm^{-1} is the difference between the transition 5/2 to 7/2 and the transition 9/2 to 9/2 and therefore should be $3.5 \times 0.137 - 4.5(0.168 - 0.137)$ or 0.340 cm^{-1}. By continuing in the same manner for the remaining two intervals, the complete calculated pattern is obtained. These calculated intervals and the observed intervals are shown for comparison in Fig. 3. Also in Fig. 3 are recorded the

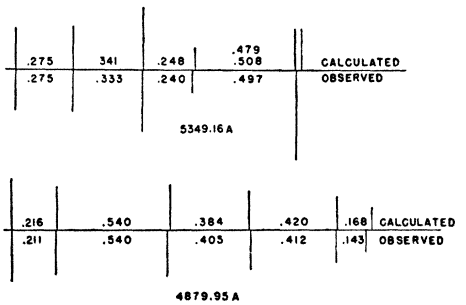

FIG. 3. Comparison of calculated and observed h.f.s. for lines 5349.16A and 4879.95A.

observed and calculated intervals for a pattern that was completely resolved 4879A. In general, the agreement between calculated and observed intervals for all of the h.f.s. patterns measured was very good.

In addition to the six 3-component patterns mentioned above as $J=0$ and $J=1$ transitions, one other h.f.s. pattern was measured that had three components. This pattern is the one belonging to line 5579A and is the result of a transition between two levels with $J=1$. The interval factor for one of these levels is approximately one-tenth of the interval factor of the other and therefore this pattern is found on Fig. 2 as an unresolved one near the axis $Y=0$. The intervals between the centers of gravity of the unresolved components were calculated as 0.459 cm^{-1} and 0.591 cm^{-1}, which are in good agreement with the observed intervals of 0.447 cm^{-1} and 0.590 cm^{-1}.

In Table II are listed the interval factors as obtained from h.f.s. measurements, together with the energy-level terms and their J values. All of the F levels of the energy levels involved in the measured transition are normal with the exception of those in term 143,352.12 cm^{-1} which are inverted.

In addition to the twelve h.f.s. patterns that were measured and satisfactorily assigned to transitions between known energy levels, a graded series h.f.s. pattern having five components was measured for 4158.6A. The wave number of this transition fits fairly well in two places in the present energy-level diagram but the h.f.s. pattern does not meet the requirements of the transition characteristics. The assignment of this line is therefore in doubt.

It is expected from the theory, and has been verified for arsenic by Tolansky,[6] that the terms based on $^2P_{\frac{1}{2}}$ should have a wider structure than those based on $^2P_{1\frac{1}{2}}$ of the same configuration. This prediction is verified in the present work; the $^2P_{\frac{1}{2}}(6p)$ terms, $\nu\nu$141,555.59, 143,352.12, and 143,394.19 have been found to have considerably larger interval factors than those found by Kopferman for the $^2P_{1\frac{1}{2}}(6p)$ terms, which were all of the order of 0.03 cm^{-1}.

Among the odd terms, those arising from an s electron should have wider structure than those arising from a d electron. The two levels, $\nu\nu$122,866.03 and 163,180.20, with the largest intervals yet found in the Cs II spectrum and, each with $J=1$, may be expected to arise, respectively, from the configurations $5p^5(^2P_{\frac{1}{2}})6s$ and $5p^5(^2P_{\frac{1}{2}})7s$ or $5p^5(^2P_{1\frac{1}{2}})8s$, rather than from the d levels blended with these groups.

The tentative calculated value of the term of the normal caesium ion was given by Laporte,

[6] S. Tolansky, Proc. Roy. Soc. **A137**, 541 (1932).

Miller, and Sawyer[7] as 189, 244 cm^{-1}. If the two levels $\nu\nu$122,866.03 and 163,180.20 are the $^1P_1$ terms of the configurations $5p^5(^2P_{\frac{1}{2}})6s$ and $5p^5(^2P_{\frac{1}{2}})7s$, respectively, then application of the Rydberg formula gives a value of 202,263 cm^{-1} for the $^1S_0$ term. This new value is preferable since all the terms in the preceding paper are then positive when referred to $^1S_0$.

[7] O. Laporte, G. R. Miller, and R. A. Sawyer, Phys. Rev. **39**, 458 (1932).

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On the Spectra of Hg II and Hg III

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The structure of many lines of ionized mercury in the region 6000–2200A has been investigated by means of apparatus of high resolving power. Many of the lines have been found to possess complex structure. The structures found are presented in the form of graphs, in which approximate distances and intensities of components are given. In a few cases more exact values of the distances are indicated. From the data collected in Table I and Fig. 2 the isotope shifts in 47 energy levels of Hg II and the hyperfine structure splittings in ten of them have been roughly determined (Table II). The isotope shift and hyperfine splitting are very small for levels of the configuration $5d^{10}nx$ (where nx designates electronic orbits higher than $6s$), and quite considerable for levels of the type $5d^96snx$. In the latter case shifts of about 0.3 cm^{-1} between consecutive even isotopes Hg 200 and 202, and hyperfine splittings amounting to from 0.4 to 1.3 cm^{-1}, have been found. Some levels of the configuration $5d^{10}nx$ show perturbation in the isotope shift; the levels $15°_{3/2}$ and $25°_{5/2}$ reveal a strong perturbation of the same kind. The data collected in Table III, Fig. 3, and Fig. 4 present the results in the cases of lines for which no correct classification seems to be known. They belong, mostly at least, to Hg II, and possibly some of them to Hg III. The results show the necessity of rejecting the existing classification of these lines (Hg II and Hg III) and some of the term values previously given for Hg II by Paschen, by Naude, and by Venkatesachar and Subbaraya. A discussion taking into account also the conditions of excitation reveals many doubts about the correctness of an extension of the analysis of the spectrum of Hg III reported by Johns. The most interesting among the lines studied are lines with isotope shifts which are the highest among all known spectra, and most of which at the same time possess no observable hyperfine structure. Since a discussion shows that probably they do not belong to Hg III, their presence furnishes evidence for the existence of two previously unknown sets of levels in Hg II, belonging to configurations $5d^86s^2nx$ and $5d^9nxn'x'$, by which the presence of a considerable number of hitherto unclassified lines can be understood.

INTRODUCTION AND EXPERIMENTAL

SPECTRA of most of the elements have been investigated for hyperfine structure and isotope shift. Astonishingly enough, the spectra of singly and multiply ionized mercury have not been studied, although the spectrum of neutral mercury has been the object of many studies. Only in the singly ionized mercury spectrum has the structure of a few lines (λ7945; 6150, 4797, 3984, 2848, and 2262) been reported before. This lack of data was undoubtedly connected with the difficulty of obtaining these spectra with high intensity. On the other hand, the study of line structures in these spectra is interesting not only for itself, but is promising also as a means of determining the classification of lines of unknown origin.

The present writer in the spring of 1939 succeeded in obtaining at the Institute of Theoretical Physics, Joseph Pilsudski University, a spectrum of singly ionized mercury of extremely high intensity. The source of light consisted of a hollow cathode discharge tube operated at a very low pressure of helium. The details of the construction of this tube have been described fully in a former paper[1] in which results of other experiments carried out with the same tube have been reported. By using different Fabry-Perot etalons,

* A great part of the experimental work was done at the Institute of Theoretical Physics, Joseph Pilsudski University, Warsaw (Poland).

[1] S. Mrozowski, Phys. Rev. **58**, 332 (1940).