HYPERFINE STRUCTURE OF SOME Hg II LINES.

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Introductory.

WHILE the hyperfine structure of the arc spectrum of mercury has been satisfactorily interpreted on the basis of nuclear spin and isotope shift, analysis of the spark lines has not progressed possibly because most of the significant lines lie in the ultra-violet region. Schüler and his collaborators[1] and Murakawa[2] have computed the even isotope shift in the level $5d^9\ 6s\ {}^2D_{5/2}$, and the latter author has given a tentative level scheme for λ 3984 Å. In the cases of thallium and lead it has been found that the spark line analysis gives g(I) values agreeing with those obtained from a study of the arc lines. The present paper is concerned with the hyperfine structure study of some prominent mercury spark lines in the ultra-violet.

Experimental.

The source employed for the study of λ 3984 Å is a low density long column arc about 70 cms. long with a current density of about 2 amps. per sq.cm. The axial radiation from the lamp gives the line λ 3984 Å intensely, and neither its structure nor the relative intensity of the components is affected in the long column radiation due to the possible complications arising from self-reversal : this fact has been specially established by a study of the photograms of the structure patterns of the line emitted from both the long column and the thin layer arcs. The lines λ 2847 Å and λ 2262 Å are examined in a hollow cathode of molybdenum with a discharge current of 100 ma. at 1000 v. in an atmosphere of helium at a pressure of about 2 mms. of mercury. Under these conditions, the hyperfine components of HgI λ 4078 Å come out sharp with correct relative intensities ; this test ensures the absence of self-reversal and widening of the satellites in the source. The Hilger E1 Quartz spectrograph is used for the preliminary dispersion. A Fabry-Perot etalon (made by Herr Lesche of Potsdam) with interchangeable invar distance pieces is employed in the study of λ 3984 Å ; a

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[1] *Ergebn. exak. Naturwiss*, **XI**, p. 167, 1932.

[2] *Sc. Pap. I.P.C.R.*, **18**, 302, 1932.

final photograph is also obtained using a quartz Lummer plate 3·45 mms. thick and 20 cms. long. This Lummer plate is the only high resolving power instrument at our disposal suitable for the examination of λ 2262 Å while in the case of λ 2847 Å, two other quartz Lummer plates of thickness 7·44 mms. and 11 mms. are employed in addition.

Results.

The lines exhibit the following structure in cm^{-1} and the eye-estimates of relative intensity are included in brackets.

λ 3983·96 Å ($5d^9\,6s^2\;{}^2D_{5/2} - 6p\;{}^2P_{3/2}$)

Murakawa	Authors
~ + 1·950 (1)	....
+ 0·958 (19)	+ 0·956 (15)
....	+ 0·879 (10)
+ 0·500 (24)	+ 0·505 (25)
+ 0·372 (7)	+ 0·380 (5)
....	+ 0·327 (6) (diffuse)
0·000 (34)	0·000 (30)
− 0·502 (7)	− 0·501 (7)

λ 2847·67 Å ($6p\;{}^2P_{3/2} - 7s\;{}^2S_{1/2}$)

~ + 0·100 (4) (Appears only as a wing of 0·000)
0·000 (20)
−0·168 (1)

λ 2262·33 Å ($5d^9\,6s^2\;{}^2D_{5/2} - 5d^9\,6s6p\;{}^2D_{5/2}$)*

+0·180 (3)
0·000 (10)
−0·193 (12)
−0·400 (8) (Exhibits a wing towards the shorter wave-length side.)

Theoretical.

Goudsmit (*Phys. Rev.*, **43**, 636, 1933) has developed the following approximate formulæ for the calculation of nuclear magnetic moments from the observed hyperfine structure interval factors; for s-electrons:

$$g(I) = \frac{3a}{8R\alpha^2} \times \frac{n_0^{\,3}}{Z_i\,Z_0^{\,2}} \times \frac{1838}{K(\frac{1}{2},Z_i)},$$

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* Venkatesachar and Subbaraya, *Zeits. f. Physik*, **73**, 413, 1931.

and for non-s-electrons :

$$g(I)=\frac{aZ_i}{\Delta\nu}\times\frac{j\,(j+1)\,(l+\frac{1}{2})}{l\,(l+1)}\times\frac{\lambda\,(l,\,Z_i)}{k\,(j,\,Z_i)}\times 1838,$$

where

$$k\,(j,\,Z_i)=\frac{4j\,(j+\frac{1}{2})\,(j+1)}{(4\,\rho^2-1)\,\rho},\ \text{where}\ \rho^2=(j+\tfrac{1}{2})^2-(\alpha Z_i)^2,\ \text{and}$$

$$\lambda\,(j,\,Z_i)=2\,l\,(l+1)\,\frac{\sqrt{(l+1)^2-(\alpha Z_i)^2}-1-\sqrt{l^2-(\alpha Z_i)^2}}{(\alpha Z_i)^2}.$$

The interval factors of 7s $^2S_{\frac{1}{2}}$, 6p $^2P_{3/2}$ and 5d^9 6s^2 $^2D_{5/2}$ in the spark spectrum calculated from the above formulæ assuming the g(I) values of Hg_{199} and Hg_{201} as 1·1 and −0·41 respectively are given in the following table :

Level	Interval Factor		Total Separation	
	Hg_{199}	Hg_{201}	Hg_{199}	Hg_{201}
7s $^2S_{1/2}$ ..	0·300	0·112	0·300	0·224
6p $^2P_{3/2}$ ..	0·025	0·009	0·050	0·056
5d^9 6s^2 $^2D_{5/2}$ ..	~0·038	~0·014	~0·114	~0·127

In the case of 5d^9 6s6p $^2\bar{D}_{5/2}$, the experimental results suggest that its interval factor is probably small. It must, however, be remembered that the $^2\bar{D}_{5/2}$ term has been examined only in connection with the analysis of λ 2262 Å; and because of the fact that in this region 0·001 Å = 0·019 cm.$^{-1}$, even a considerable separation of the level may lie beyond the resolving power of the apparatus used. Assuming the interval factors obtained above, the calculated structure of the lines agrees as well as could be expected with the observed values.

Discussion.

(1) λ 2847 Å: The resolution of this line is incomplete. The satellite −0·168 cm.$^{-1}$ is due to Hg_{199} and arises from an ff-transition 0→1 (4·11 per cent.); the transitions 1→1, 2 (12·34 per cent.) give rise to the wing of the main line estimated to extend to about +0·100 cm.$^{-1}$. Hg_{201} contributes about 5·13 per cent. more to this wing in the transitions 1→0,1,2, and it is to be assumed that the components 2→1, 2, 3 lie close to the main line on the longer wavelength side. Thus the wing with a total intensity of 17·47 per cent. is nearly four times brighter than the satellite −0·168 cm.$^{-1}$ (4·11 per cent.); and this agrees with the observed ratio of the intensities.

(2) λ 3984 Å : Previous investigators, who have analysed this line, conclude that the satellite at $+0\cdot956$ cm.$^{-1}$ is single. Our analysis has revealed a close doublet character in this satellite ; we have therefore resolved the two components completely and measured them separately. Assuming the calculated interval factors, we obtain the following scheme of levels which gives a structure pattern agreeing with the observed one.

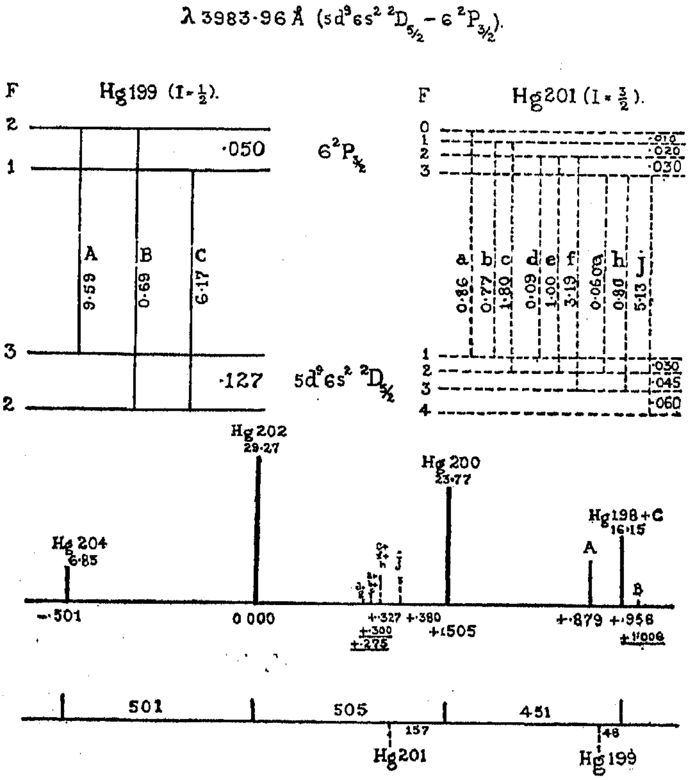
λ 3983·96 Å $(5d^9 6s^2\ ^2D_{5/2} - 6\ ^2P_{3/2})$.

FIG. 2.

Thus theory and experiment agree in giving the total spin separations as $0\cdot050$ cm.$^{-1}$ and $0\cdot120$ cm.$^{-1}$ for the two levels 6 $^2P_{3/2}$ and $^2D_{5/2}$ respectively ; but Murakawa gives such large separations as $1\cdot578$ cm.$^{-1}$ and $0\cdot992$ cm.$^{-1}$ respectively which lead to abnormal values of the g(I) factors. This difference arises partly from the fact that Murakawa has observed a satellite at about $+1\cdot950$ cm.$^{-1}$ which we have not been able to confirm.

(3) λ 2262 Å : The observed structure of this line is mainly due to the even isotope shift. But as the intensity relations do not agree with the relative abundance of the even isotopes, the influence of the odd isotopes also has to be considered in the interpretation of the structure of the line. The wing of the satellite $-\ 0\cdot400$ cm.$^{-1}$ has to be interpreted as a close satellite belonging to Hg_{199} and as a consequence $-0\cdot193$ cm.$^{-1}$ though

more intense than 0·000 has been ascribed to Hg_{202}, the intensity excess being assumed to have been caused by the superposition of the close satellites of Hg_{201}. This allocation of the satellites gives for $^2\overline{D}_{5/2}$ an even isotope displacement of about 0·680 cm.$^{-1}$ The structure of the line can then be explained by the following scheme of levels :

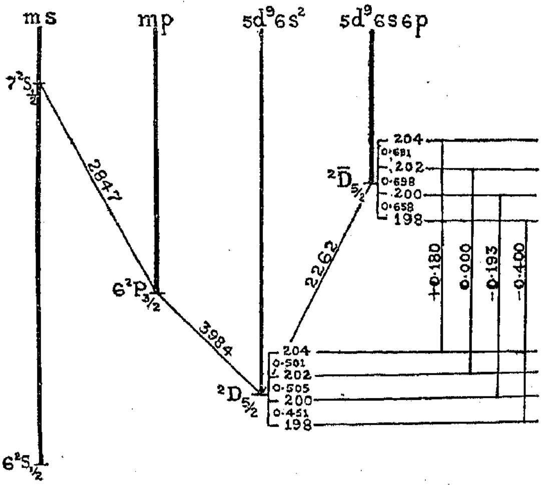

Fig. 3.

The following alternative interpretation of the structure of λ 2262 Å, which at first sight seems to be more direct, cannot be reconciled with the greater intensity of −0·400 cm.$^{-1}$ as compared with −0·180 cm.$^{-1}$.

		Theoretical Intensity of even isotopes only	Observed Intensity
+0·180	Hg_{198}	9·98	3
0·000	Hg_{200}	23·77	10
−0·193	Hg_{202}	29·27	12
−0·400	Hg_{204}	6·85	8

The observed wing on the shorter wavelength side of −0·400 cm.$^{-1}$ cannot be explained by attributing it to the odd isotopes, because it lies near −0·400 cm.$^{-1}$ ascribed to Hg_{204} and is the only extra satellite observed. The intensity anomaly will be further enhanced if Hg_{199} and Hg_{201} are considered as being superposed on Hg_{198} and Hg_{200} respectively.

The present theory of the even isotope displacement is not adequate to enable us to account for the variation in the displacements on passing from $5d^9$ 6s 6p $^2\overline{D}_{5/2}$ to $5d^9$ 6s $^2D_{5/2}$. While the levels 7s $^2S_{1/2}$ and 6p $^2P_{3/2}$ exhibit little isotope displacement, the levels $^2\overline{D}_{5/2}$ and $^2D_{5/2}$ show large displacements. Another fact of importance that emerges out of the analysis of λ 3984 Å is that the even isotope separations are not exactly equal for a given level. Though Hg_{204}, Hg_{202} and Hg_{200} are nearly equally separated

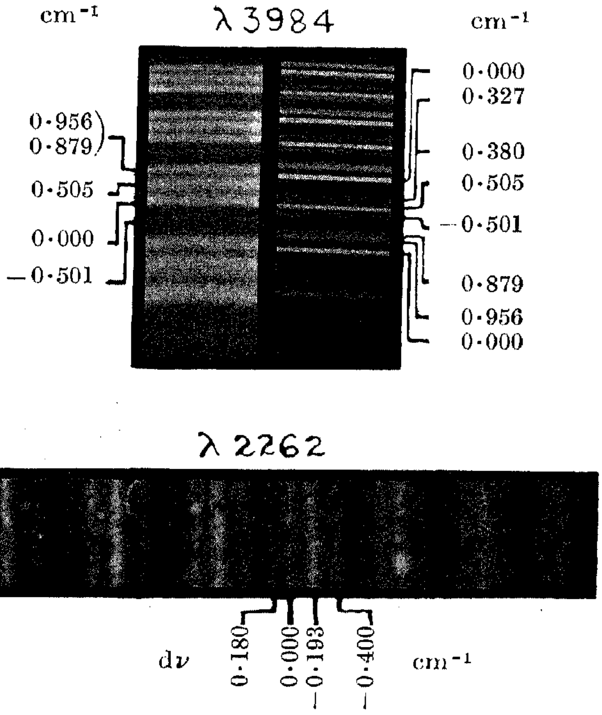

FIG. 1.—λ 39 4 Å : *Left*—Pattern obtained by a Fabry-Perot etalon with an air gap of 2·5 mms.

Right—Pattern obtained by a Lummer-Gehrcke plate of thickness 3·45 mms. and length 20 cms.

λ 2262 Å : Pattern obtained by the above Lummer-Gehrcke plate.

by about 0·500 cm.$^{-1}$, Hg_{200} and Hg_{198} are separated by only 0·451 cm.$^{-1}$ in $^2D_{5/2}$. Even the ground level 6 $^1S_0$ of the arc spectrum of mercury shows such varying differences between successive even isotopes. The analysis of λ 3984 Å reveals yet another interesting fact that the separation between the centres of gravity of Hg_{199} and Hg_{201} is greater than the even isotope displacement; this is seen to be true even in some mercury arc lines such as λ 2536 Å.

The isotope displacements in Zn II, Cu I, W I, Pb I and Pb II are positive, *i.e.*, the heaviest isotope lies deepest. In Cd II, Hg I and Hg II the isotope displacement is negative. The nuclei of these elements contain no proton and consist only of α–particles and neutrons. According to the following table, elements whose nuclei contain an odd number of α–particles exhibit positive isotope shift and those with even number a negative displacement.

	+	−
Zn	15α	..
Cd	..	24α
W	37α	..
Hg	..	40α
Pb	41α	..

Molybdenum has been omitted from the above table, since Grace and More (*Phys. Rev.*, **45**, p. 168, 1934) who have analysed the Mo I lines consider their " interpretation of the results somewhat uncertain". The nuclei of Cu as well as Tl contain one proton and the arc spectra of these elements exhibit a positive isotope displacement. The Tl II spectrum shows a negative shift and it would therefore be of interest to investigate whether Cu II also behaves similarly.