The Hyperfine Structure Intensities of the $2^3S_1-2^3P_{0,\,1,\,2}$ Triplet in Optically Excited Mercury Vapor

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The hyperfine structures of the mercury lines 5461, 4358 and 4047 in fluorescence emission were obtained in the second order of a 30,000 line, 21 ft. grating. The ratio of the intensity of the central component to the intensity of any one of the other components was found greater than a similar ratio for the emission from the exciting arc. This anomalous increase in intensity of the central component in fluorescence may be accounted for by making use of the absorption coefficients of the components of 4047.

INTRODUCTION

THE hyperfine structure of the visible triplet 5461, 4358 and 4047 of mercury emitted from optically excited fluorescent mercury vapor was first investigated by Collins.[1] With a Lummer-Gehrcke plate he found that 5461 for pure mercury consisted of the central component only, while with a few millimeters of nitrogen admixture, the central and the $+0.785$ cm^{-1} components appeared with about equal intensity. The lines 4358 and 4047 also were observed to have peculiar component intensities as compared with those of the arc.

More recently Mrozowski[2] also using a Lummer-Gehrcke plate and similar experimental set-up, observed for these three lines in fluorescence, the central component only.

In the experiment reported on in this paper the above-mentioned lines were observed in the second order spectrum of a 30,000 line, 21 ft. grating.

APPARATUS AND PROCEDURE

The quartz resonance tube about 2.5 cm diameter and 25 cm long was of the conventional horn-shaped design. The total radiation from two water-cooled and magnetically deflected quartz mercury arcs* excited the mercury vapor in the resonance tube. The admixed nitrogen was kept moving slowly through the resonance tube and over P_2O_5 and hot copper and copper oxide. The temperature of the resonance tube was about 25°C. Photographic exposures ranged from one quarter to sixty hours, and the temperature of the grating was constant to less than 0.1°C. The shorter exposures were sufficient when a telephoto lens was used near the photographic plate.[3] Eastman 33 plates were used for 4047 and 4358, while G 1 and G 3 plates were used for 5461. The plates were put in a small prism spectrograph and density markings put on by the help of calibrated screens.[4] Density measurements were made by a photoelectric densitometer[5] particularly designed for hyperfine structure work. The ratio of the intensity of the central component to that of some other component for the fluorescence was compared with the like ratio for the exciting arc. The arc used as comparison was a water-cooled Uviarc running at three amperes. Since for an optimum photographic density the exposure time for the arc was a few seconds while that for the fluorescence was several hours, it was necessary to investigate a possible change in the contrast for such large differences in instantaneous energy falling on the plate. It was found[6] that when the intensity was increased by a factor of about 10,000 the ratio of a strong line to a weak line increased by a factor of about 1.3. This factor, though smaller than expected, has been incorporated in Table I.

[1] E. Hobart Collins, Phys. Rev. **43**, 753 (1928).

[2] S. Mrozowski, Zeits. f. Physik **78**, 826 (1932).

* Cooper-Hewitt Uviarc, horizontal type.

[3] J. B. Green, Phys. Rev. **37**, 473 (1931).

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

[5] G. A. Rosselot built this photoelectric densitometer using two FP54 tubes.

[6] C. E. Hesthal and V. C. Wilson kindly made these measurements for us.

TABLE I. *Observed intensity quotients for fine structure components of Hg 4047, 4358 and 5461. These quotients represent the ratio of the intensities of the components to the intensity of the central component in fluorescence divided by the corresponding ratios for the arc.*

4047	Pressure N_2 (mm)	Exposure (hrs.)	+0.330, +0.270 (cm^{-1})	−0.394 (cm^{-1})	−0.743 (cm^{-1})	
	0	43	2.9	2.8	2.9	
	3.7	59	2.9	2.9	—	
	8.0*	36	3.5	2.0	—	
	27.7	21	2.0	—	—	
	41.8*	20	2.5	—	—	
4358			+0.836	+0.505, +0.566	−0.240	−0.555
	3.7*	59	7.0	2.9	—	—
	8.0	36	5.5	2.3	2.8	3.8
	15.5	24	—	3.2	3.8	—
	15.9	¼	—	4.5	—	—
	42.0	19	—	4.1	—	—
5461			+0.790	−0.278		
	3.7	46	—	3.6		
	8.4*	34	3.4	—		
	15.5	24	—	2.3		
	39.2	22	—	4.4		

* These exposures are reproduced in Figs. 1, 2, 3, 4.

In order to test for scattered and reflected light there was placed between each arc and the resonance tube a glass plate which cut out the 2537 exciting line, thus terminating all resonance radiation, but which passed the visible triplet. After 20 hours, not a trace of even the central component was visible.

Results

Typical photographs of the fine structure of λ4047, 4358 and 5461 in the arc and in fluorescence are shown in Figs. 1, 2, 3 and 4. In Table I are presented the essential details of the exposures together with the results of the intensity measurements. The "intensity quotients" represent the ratio of the intensity of the particular component to the intensity of the central component in fluorescence divided by the same ratio in the arc.

Discussion

We have not been able to correlate the findings of Collins with those reported here. We were successful in obtaining only one measurable plate at zero nitrogen pressure, but except for a marked decrease in intensity of emission there seemed to be no marked difference in hyperfine structure intensity ratio whether nitrogen was present or not. Perhaps Mrozowski did not get components other than the central one because of insufficient exposure.

One should expect components in fluorescence as is evident from Fig. 5.[7] In the exciting source all the components are present and each with its absorption coefficient would contribute to its component in emission. In order to calculate the relative intensities of the components in emission it will be necessary to make use of the fact that the central component of 4047 has a much larger absorption coefficient than any of the other components, and that the other components have absorption coefficients that decrease with decrease in intensity of the component.[8]

A detailed account of the process involved is probably as follows: The components of 2537 put the various isotopic mercury atoms into the 2^3P_1 state. Since the absorption coefficients of the various components of 2537 are probably different, the relative concentrations of the isotopes in this state will not be the same as the relative number in the ground state. This concentration may be further modified by collisions of the second kind with nitrogen resulting in mercury being left in the metastable 2^3P_0 state. It is not necessary to know the relative number of isotopes in this 2^3P_0 state, since the linear absorption coefficients for the various components of 4047 have been measured for just such a concentration. From this metastable state the populating of the 2^3S_1 state will depend upon the absorption of 4047, the component with the greatest absorption contributing the most. The absorption of 4358 and 5461 is negligible.[9] For example the lower hyperfine level of the 2^3S_1 state of the 199 mercury isotope is populated by the -0.743 cm^{-1} component of 4047. There is no transfer of energy between the various isotopes because each isotope is isolated from all others for the life time of the 2^3S_1 state by the admixed

[7] Compiled from H. Schuler and J. E. Keyston, Zeits. f. Physik **72**, 423 (1931).

[8] M. L. Pool and S. J. Simmons, Phys. Rev. **43**, 1045 (1933).

[9] M. L. Pool and S. J. Simmons, Phys. Rev. **42**, 909 (1932).

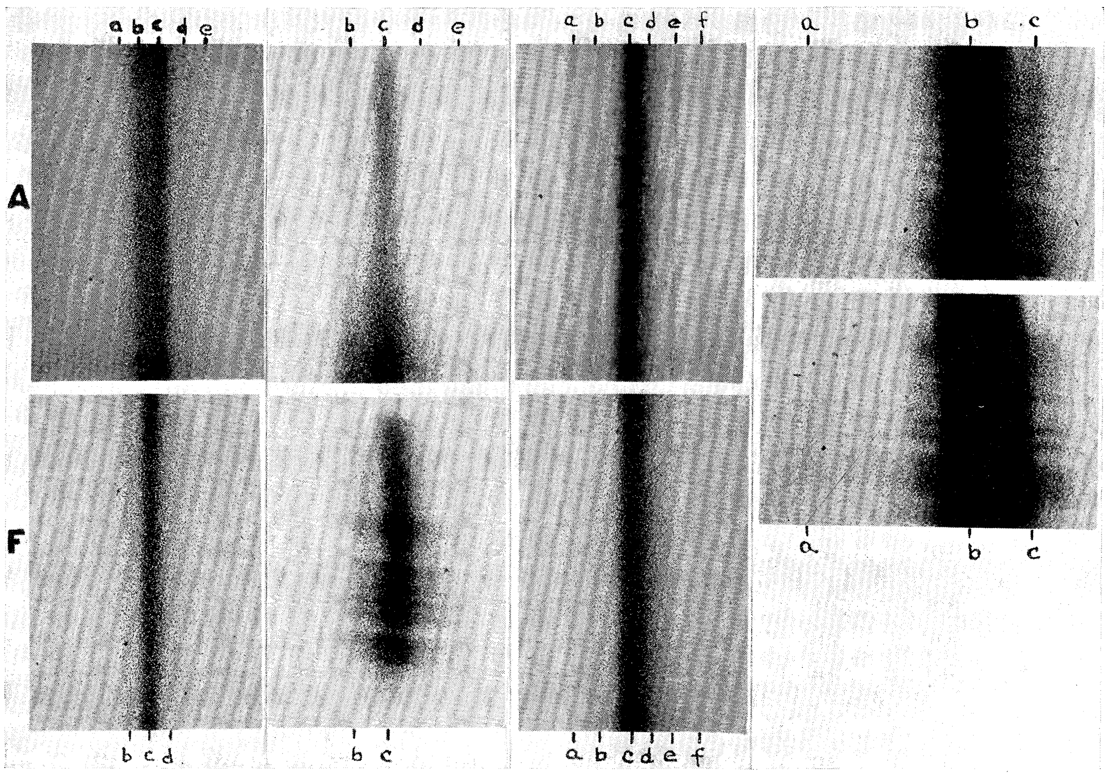

FIG. 1 FIG. 2 FIG. 3 FIG. 4

FIG. 1. The second order of λ4047 enlarged 50 times. A stands for arc and F for fluorescence. The components are a, $+0.668$; b, $+0.270$ and $+0.330$; c, 0; d, -0.394; e, -0.743 cm^{-1}.

FIG. 2. Second order of λ4047 as obtained with an additional telephoto lens near the plate.

FIG. 3. Second order of λ4358 enlarged 50 times. The components are a, $+0.836$; b, $+0.505$ and 0.566; c, 0; d, -0.240; e, -0.555; f, -0.960 cm^{-1}.

FIG. 4. Second order of λ5461 enlarged 50 times with telephoto lens in front of plate. The components are a, $+0.790$; b, 0; c, -0.278 cm^{-1}.

nitrogen. There also seems to be little chance of transfer of energy between the hyperfine levels of a given odd isotope.

In column three of Table II are listed the linear absorption coefficients. In column four are the values of $1-e^{-\mu}=A$ which are proportional to the total absorption of a particular component. These absorbed energies would give the relative concentrations in the various corresponding hyperfine levels of the $^3S_1$ state, see Fig. 5. The volume optically excited is approximately a two centimeter cube. In column five are the quotients, Q, formed by dividing the A of the central component by the A's of column three. This quotient shows how much larger the ratio of the intensity of the central component to some other component in fluorescence is than a similar ratio in the exciting arc. As may be seen from Fig. 5, the first Q in Table II for each of the three

TABLE II. *Calculated intensity quotients.*

Pressure N_2	Component	μ	A	Q	Q'
2 mm	0 cm^{-1}	0.101	0.105		
	+0.330, +0.270	.036	.036	2.9	2.7
	− .394	.024	.024	4.4	4.0
	− .743	.010	.010	10.5	9.5
10 mm	0 cm^{-1}	.138	.130		
	+0.330, +0.270	.049	.045	2.9	2.6
	− .384	.036	.035	3.7	3.4
	− .743	.022	.021	6.2	5.5
40 mm	0 cm^{-1}	.164	.153		
	+0.330, +0.270	.054	.052	2.9	2.6
	− .394	.040	.039	3.9	3.5
	− .743	.028	.027	5.7	4.9

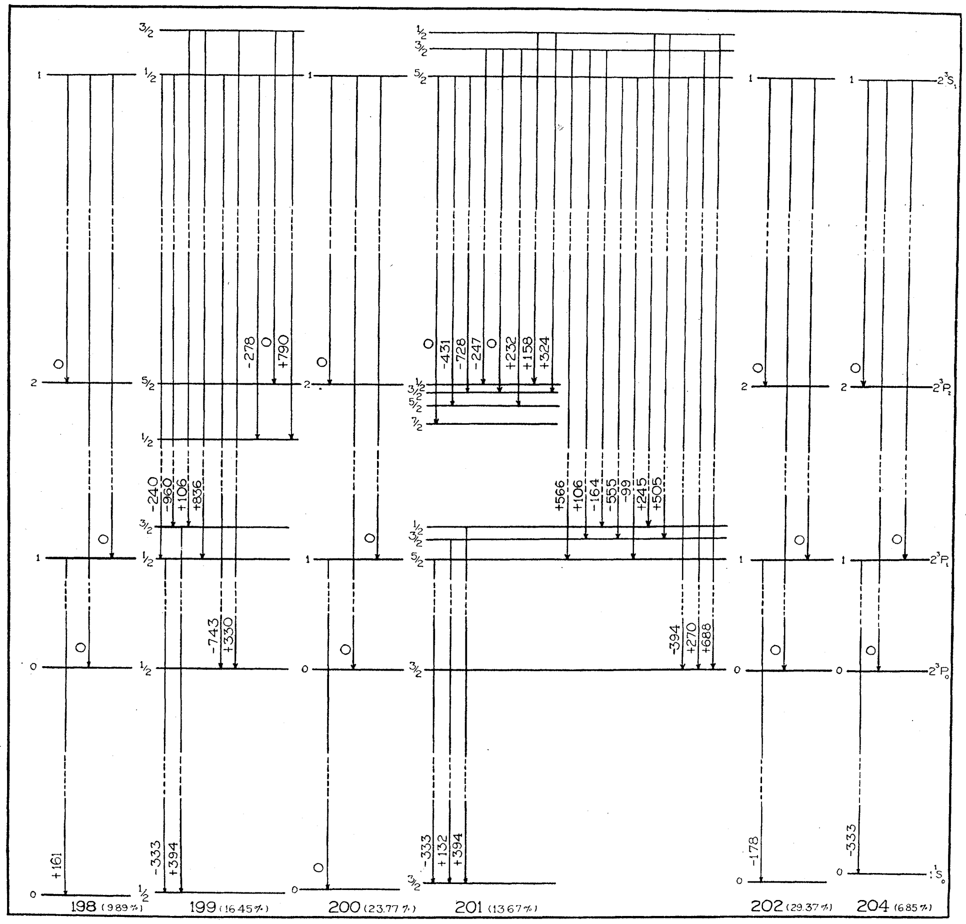

FIG. 5. Hyperfine energy level diagram of mercury.

nitrogen pressures applies to the $+0.566$ cm^{-1} component of 4358 and the $+0.790$ cm^{-1} component of 5461; the second Q applies to the -0.555 cm^{-1} of 4358; and the third to the -0.278 cm^{-1} of 5461 and -0.960 and -0.240 cm^{-1} of 4358. However, for the components of 4047 there is reabsorption, and the above quotients will be modified slightly as shown in column five. It is seen that the values of Q' of Table II compare favorably with the quotient values for 4047 in Table I and the values of Q in Table II are also reasonable with those for 4358 and 5461 in Table I.

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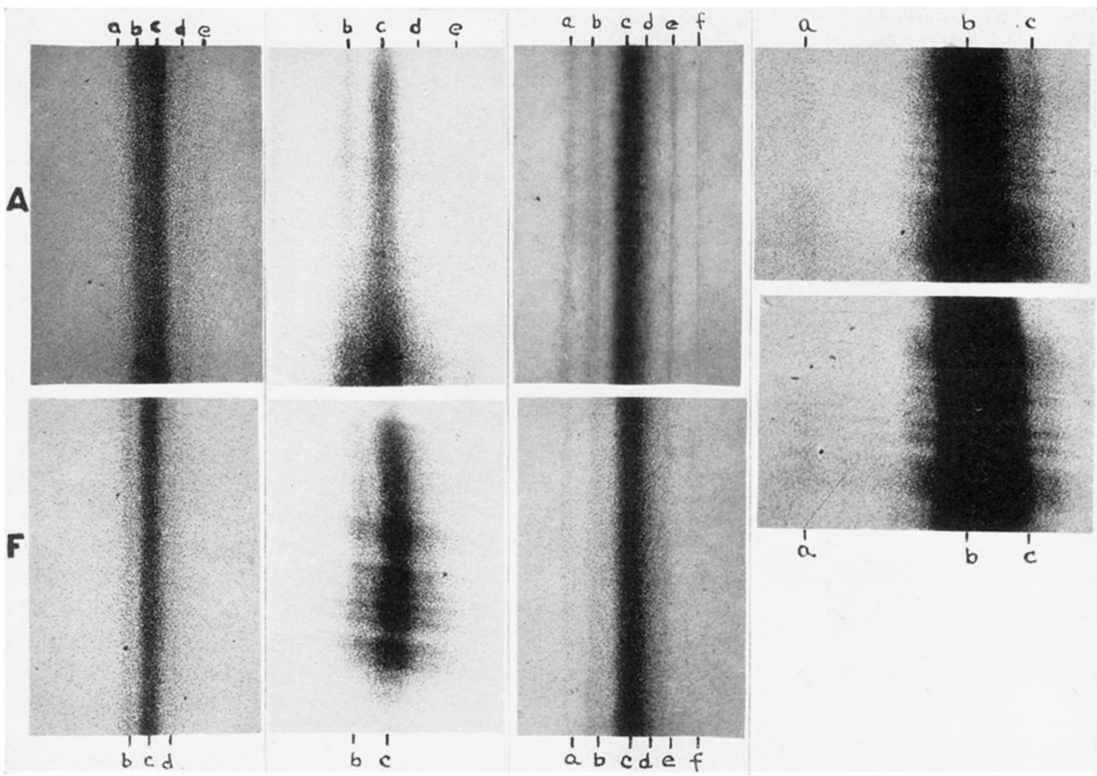

FIG. 1 FIG. 2 FIG. 3 FIG. 4

FIG. 1. The second order of $\lambda 4047$ enlarged 50 times. *A* stands for arc and *F* for fluorescence. The components are *a*, $+0.668$; *b*, $+0.270$ and $+0.330$; *c*, 0; *d*, -0.394; *e*, -0.743 cm^{-1}.

FIG. 2. Second order of $\lambda 4047$ as obtained with an additional telephoto lens near the plate.

FIG. 3. Second order of $\lambda 4358$ enlarged 50 times. The components are *a*, $+0.836$; *b*, $+0.505$ and 0.566; *c*, 0; *d*, -0.240; *e*, -0.555; *f*, -0.960 cm^{-1}.

FIG. 4. Second order of $\lambda 5461$ enlarged 50 times with telephoto lens in front of plate. The components are *a*, $+0.790$; *b*, 0; *c*, -0.278 cm^{-1}.