THE FINE STRUCTURE OF THE SHARP SERIES TRIPLET, $2^3P_{0,1,2}-2^3S_1$, OF OPTICALLY EXCITED MERCURY RADIATION

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Abstract

Measurements on the fine structure of the sharp series triplet, lines of wave-lengths λλ5461, 4358 and 4047 were made with two Lummer-Gehrcke plates under two conditions of optical excitation. The first condition of optical excitation was obtained by having mercury vapor only in the resonance tube, giving excitation by absorption of λ4358, the second by having mercury vapor with nitrogen present at a pressure of 2 to 4 mm, giving excitation by absorption of both λ4358 and λ4047. For the first condition of excitation the wave-length differences in milli-angstroms are for λ5461, $d\lambda 0$; for λ4358, $d\lambda -157$, -107, -20, 0, $+30$, $+46$, $+183$; for λ4047, $d\lambda -116$, -62, -52, 0. For the second condition the wave-length differences are for λ5461, $d\lambda -235$, 0; for λ4358, $d\lambda -107$, -20, 0, $+30$, $+183$; for λ4047, $d\lambda -110$, -62, -53, 0. Certain fine structure energy differences of interest in the construction of energy diagrams are pointed out but it was not found possible with the data available to construct a complete energy diagram of the triplet. A comparison of the fine structure observed under the two conditions of optical excitation with one another and with the fine structure of the arc shows striking differences which make it evident that differences in fine structure exist which depend on the method of excitation.

Introduction

There is at present no theory which offers a completely satisfactory explanation of the fine structure of the spectral lines. Ruark and Chenault[1] have proposed the introduction of a fifth or fine quantum number and a selection principle to account for certain fine structures. However, they have proposed no kinematical interpretation of this fine quantum number, unless we accept a vague suggestion that it may be associated in some way with differences in configuration of the underlying electron shells. More recently MacNair[2] and Fraulein Schrammen[3] have devised energy levels which account in a satisfactory way for their observations on the fine structure of a large number of cadmium lines. These level schemes, however, have not been unique and at present there is no way of deciding among the various possibilities.

Pauli[4] has suggested that an appropriate moment associated with the nucleus of the atom may account for some types of fine structure. He has also pointed out that such a model would imply the existence of phenomena of the same nature as the Paschen-Back effect, and in support of this has cited Nagaoka's observations on the Zeeman effect of the $2^3P_{0,1,2}-2^3S_1$

[1] Ruark and Chenault, Phil. Mag. **50,** 937 (1925).
[2] MacNair, Phil. Mag. **2,** 613 (1926).
[3] Schrammen, Ann. d. Physik **83,** 1161 (1927).
[4] Pauli, Naturwissenschaften **12,** 741 (1924).

mercury triplet. Back and Goudsmit[5] have shown that the fine structure of the bismuth spectrum and its very complex Zeeman effect may be successfully accounted for if it is assumed that the bismuth nucleus possesses a mechanical moment of $(9/2)(h/2\pi)$. It does not appear, however, that the fine structure of the mercury spectrum is to be accounted for in this way. Goudsmit[6] has pointed out that on the nucleus spin hypothesis $\lambda 2537$ should have at most three components and that these should show three types of Zeeman effect in weak fields. Actually the line has five components, three of which show a 3/2 normal Zeeman effect.

The primary object of the present investigation was to learn whether fine structure patterns could be made to vary by changing the method of excitation. It was not expected that the method used would be adapted to accurate determination of wave-length differences, because of the long exposures required and the impairment of definition in the interference patterns of the Lummer-Gehrcke plates occasioned by slight and almost unavoidable temperature changes. The results of Nagaoka[7] (the data used by Ruark[8]) for the fine structure of these lines in the ordinary arc were accepted, and an attempt was made to identify the various components observed with one or another of the accepted patterns. In general this succeeded very well, the observed wave-length differences agreeing quite closely with those found by Nagaoka.

The possibility of different methods of excitation was provided by some beautiful experiments of Fuchtbauer,[9] upon the optically excited spectrum of mercury. These experiments were later greatly amplified and extended by R. W. Wood,[10] who showed, for example, that there were several ways of raising an electron to the 2^3S_1 level by optical means. The experiments now presented show that the fine structure of the lines emitted when the electron falls to the $2^3P_{0,1,2}$ levels are different for the different ways in which the electron may be raised to the 2^3S_1 level initially.

The two conditions of optical excitation, under which the fine structure of the $2^3P_{0,1,2}-2^3S_1$ triplet has been observed, are:

A. Absorption by mercury vapor in the absence of any foreign gases;

B. Absorption by mercury vapor in the presence of nitrogen at a pressure of from 2 to 4 mm of mercury.

Under the condition A the 2^3S_1 level is reached by the absorption of $\lambda 2537$ followed by the absorption of $\lambda 4358$. Absorption of $\lambda 4047$ and $\lambda 5461$ is negligible.[10]

Under condition B some electrons reaching the 2^3P_1 level are spilled over into the 2^3P_0 level by collision with nitrogen molecules and the concentration

[5] Back and Goudsmit, Phys. Rev. **31,** 1125 (1928).

[6] Letter from Dr. S. Goudsmit.

[7] Nagoaka, Proc. Phy. Soc. London, **39,** 91 (1917).

[8] Ruark, Phil. Mag. **1,** 980 (1926).

[9] Fuchtbauer, Phys. Zeits. **21,** 635 (1920).

[10] Wood, Proc. Roy. Soc. **A106,** 679 (1924); Phil. Mag. **50,** 774 (1925) and Phil. Mag. **4,** 466 (1927).

of atoms in this metastable state becomes great enough that the absorption of λ4047 is as great or greater than that of λ4358. Absorption of λ5461 is still negligible. Under this condition, then, electrons reach the 2^3S_1 level from either the 2^3P_1 or the 2^3P_0 level. There is also evidence[11] that some electrons may reach the 2^3S_1 level directly from the 3^3D levels and it appears that this process plays an important role in the interpretation of results.

Apparatus

The general arrangement of apparatus is shown in Fig. 1. The resonance tube A was a quartz tube one inch in diameter and about six inches long, sealed by a graded seal to a Pyrex tube of the same diameter. It was made horn shaped to minimize reflected light and was painted black except for a two inch space which admitted light from two mercury arcs. Self reversal of the lines emitted by the exciting arcs was avoided by water-cooling these and by forcing the discharge close to their walls by means of two small magnets. The end of the resonance tube was sealed by a carefully polished disk of fused quartz cut to fit the inner diameter of the tube. By means of a pointed oxygen-hydrogen flame the walls of the tube and the end of the disk were heated and fused together. Care was taken to keep the center of the inner surface of the quartz plate undisturbed and free from any deposit of oxide caused by the hot flame. After the seal was made and tested, the outside of the quartz was ground and polished again.

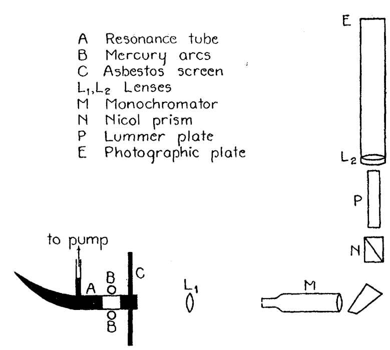

Fig. 1. Arrangement of apparatus.

The end of the tube was painted black except for an aperture of such size that no scattered light from the walls of the tube could enter the lens L_1 which focused the light on the collimator. An asbestos screen C kept direct light from the arcs from entering the rest of the apparatus.

The optically excited radiation was focussed on the collimator slit of a Hilger monochromator M. For most of the measurements the lens and slit of the telescope were removed and the parallel beam of light from the prism of the monochromator passed directly through a nicol prism into the Lummer-Gehrcke plate. A less satisfactory method was to use the telescope and second slit of the monochromator, with a cylindrical lens placed at its focal distance from the slit with its axis parallel to the slit, so that it rendered the emergent rays parallel in the plane of the Lummer-Gehrcke plate and made possible the focussing of the slit of the monochromator on the photographic plate.

The Lummer-Gehrcke plate was placed in a horizontal position with just sufficient tilt to bring the maximum of intensity into the lower orders

[11] Wood, Phil. Mag. **4,** 480 (1927).

of the interference pattern. Back of the Lummer-Gehrcke plate an achromatic lens focussed the light onto a photographic plate. The Lummer-Gehrcke plate and camera were rigidly mounted on a five inch "I" beam.

The Lummer-Gehrcke plates were those used by Ellett and MacNair.[12] Their thicknesses and order separations are given in Table I below.

TABLE I. *Data relative to the Lummer-Gehrcke plates.*

Plate	Thickness (cm)	Order separations λ5461	λ4358	λ4047
1	0.642	0.189A	0.117A	0.101A
2	0.492	0.248A	0.153A	0.131A

All the apparatus was mounted in a constant temperature room. For exposures of less than six hours the extreme variation in temperature of the room was less than 0.2°C; for exposures of twenty to thirty hours, the extreme variation in temperature was less than 0.4°C. The Lummer-Gehrcke plates were insulated by several coverings to damp out the small temperature fluctuations, and their temperature, inasmuch as sharp lines were obtained certainly varied much less than that of the room.

RESULTS AND DISCUSSION

The data obtained for both conditions of excitation for the lines λ5461, λ4358 and λ4047 are given in Tables II, III and IV. The use of two Lummer-Gehrcke plates with different thicknesses made possible the determination, with considerable accuracy, of the wave-length differences. The interpretations are made more certain since, as mentioned above, we expect the components observed in the optically excited radiation to have nearly the same wave-length as those observed in the mercury arc. For purposes of comparison the fine structure of the mercury arc as observed by Nagoaka[7] is given in the first column. The intensities are merely visual estimates.

TABLE II. *Data for* λ5461.

Arc	Condition A			Condition B		
dλ Milli-Angstroms	Estimated Intensities	dλ Milli-Angstroms	dν cm⁻¹	Estimated Intensities	dλ Milli-Angstroms	dν cm⁻¹
−237				10	−235	+785
102						
70						
47						
19.9						
8.4						
0		Single		10	0	0
8.2						
18.4						
85						
128						
214						

[12] Ellett and MacNair, Proc. Nat. Acad. **13**, 583 (1927) and Phys. Rev. **30**, 180 (1928).

In Table II are given the results for the green line λ5461. This line under condition A is single; a surprising result when we consider that the fine structure of the arc line shows 12 components. A thirty-one hour exposure of a film sensitized for green by an erythrozine dye[13] gave a sharp, intense and over-exposed single component but failed to reveal other components.

In condition B there were two components of about equal intensity with a wave-length difference of 0.235A, and since this agrees within experimental error with the difference between 0 and −0.237A components of the arc, these values were assigned. The single component of condition A is then very probably the zero component of the arc line. On one spectrogram only two very weak components which could not be assigned a definite wave-length were observed. These latter may have been due to peculiar conditions existing in the source of light or possibly to a small amount of stray light.

The results for λ4358 are given in Table III. It appears from this table that only a few of the components observed in the fine structure of the mercury arc line λ4358 appear in the fine structure of the optically excited line. Most of those observed agree closely in wave-length with the published

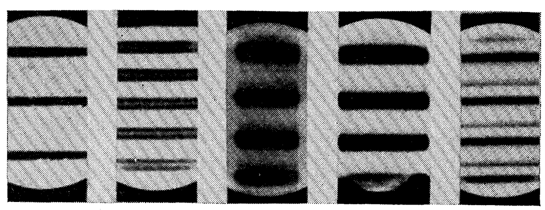

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Fig. 2. Enlargements of selected spectrograms.

measurements of the arc line. The wave-length differences assigned to the components of λ4358 in condition B are the result of measurements taken with the thin Lummer-Gehrcke plate only, the selection of wave-length differences being made so as to account for the overlapping of orders on the spectrogram taken with the thick Lummer-Gehrcke plate. (See Fig. 2d.)

The Lummer-Gehrcke patterns for λ4047 taken under the two conditions of excitation show the same lines. The measurements are given in Table IV.

Five enlargements of selected spectrograms are presented in Fig. 2. Spectrograms *a* and *b* show the appearance of the green line, λ5461, under the two conditions A and B respectively. The spectrogram *b* showing the 0 and −0.235A components was taken with the thicker Lummer-Gehrcke plate, with an order separation for λ5461 of 0.189A. With the thin Lummer-Gehrcke plate having an order separation of 0.248A the components were close together, appearing as one broad line. Spectrograms *c* and *d* show

[13] Baly, Spectroscopy Vol. II, p. 373; see also Derr, Photography for students of Physics and Chemistry, p. 102.

the appearance of λ4358 taken with the thick Lummer-Gehrcke plate under the A and B conditions of excitation. When due allowance is made for different times of exposure and different light intensity of the source it is

TABLE III. *Data for λ4358.*

Arc	Conditions A			Condition B		
Milli-Angstroms	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}
−238						
206						
160	2	−157	+.827			
108	2	107	0.560	*	−107	+.560
95						
47						
21	4	20	0.105	*	20	0.105
9						
3						
0	10	0	0	*	0	
+3						
19						
29	1	+30	−.160	*	+30	−.160
46	4	46	0.244			
108						
159						
182	3	183	0.956	*	183	0.956
224						
238						

* Due to over-lapping of orders estimated intensities uncertain.

quite evident that the intensities ratios have changed. The spectrogram *e* shows the appearance of λ4047 under condition B taken with the thin Lummer-Gehrcke plate. Only one enlargement of the spectrogram is shown

TABLE IV. *Data for* λ4047

Arc	Condition A			Condition B		
Milli-Angstroms	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}	Estimated Intensities	$d\lambda$ Milli-Angstroms	$d\nu$ cm^{-1}
−116	1	−116	+.708	1	−116	+.708
61.4	2	62	0.378	2	62	0.378
47.5	5	53	0.330	5	53	0.330
12.3						
3.9						
0	10	0	0	10	0	0
+4.1						
59.2						
117.0						

since the only change in λ4047 under the two conditions of excitation was a slight change in the relative intensities.

Fine Structure Energy Levels

Ruark[8] has given an excellent critical summary of the existent data for the fine structures of a large number of lines of the mercury arc, including λλ5461, 4358, 4047 and also λλ3663.28, 3654.83, 3650.15, 3663.05, 3131.56 and 2967. His proposed fine structure energy levels do not account for all of the fine structure components of these lines, but they do point out the existence of energy differences common to the several lines. So many of the observed fine-structure components fit into his level scheme that it seems reasonable to assume that these levels actually exist and that it would be possible to account for the remaining components by the introduction of a few additional levels, if the wave-lengths of these components were only known with the requisite accuracy. If it is assumed that this incomplete level scheme is valid as far as it goes, certain conclusions are evident. For example, absorption of either λ4358 or λ4047 should excite fine-structure levels of 2^3S_1 from which arise no less than nine components of λ5461. Now actually, as has been pointed out above, the situation is quite different, λ5461 having sometimes but one and sometimes two components when excited by absorption of these lines.

An attempt has been made to find a set of levels which would account for the existence of the fine-structure components of λλ5461, 4358 and 4047 observed in the optically excited spectrum. The fine structure of λ2537 is known to be the same when excited in resonance radiation as in the arc[14] so that we may be certain that none of the five components ascribed to this line are due to self-reversal or other perturbing causes. A frequency difference of 0.160 cm^{-1} is common to λ4358 and λ2537 and the difference 0.349 cm^{-1} found in λ4358 may be the same as 0.345 cm^{-1} observed in λ2537.

The introduction of frequency differences of 0.330 cm^{-1} into 2^3P_0 and of 0.375 cm^{-1} into 2^3S_1 accounts satisfactorily for all of the components of λ4047 in the optically excited radiation. McCurdy[15] finds a frequency difference of 0.330 cm^{-1} in λ2967, $2^3P_0-3^3D_1$.

There is obviously no way of deciding which level of 2^3S_1 gives rise to the single component of λ5461 observed under condition A, nor does the difference of 0.785 cm^{-1} between the two components observed in condition B appear in either λ4358 or λ4047. The introduction of nitrogen (condition B) does not give rise to any new components in λ4047 so that there is no reason to say that the absorption of this line in condition B causes the excitation of levels of 2^3S_1 not reached by any component of λ4358. The emission of an additional component upon admission of nitrogen is probably due to some process which gives rise to emission of λλ5461, 4358 and 4047 when mercury vapor in the presence of nitrogen is excited by bromine and chlorine filtered radiation from which these three lines are absent. Wood points out that this may be brought about by spilling electrons from the 3^3D levels

[14] Ellett and MacNair, Phys. Rev. **31,** 180 (1928).

[15] McCurdy, Proc. Nat. Acad. Sci. **13,** 701 (1927).

to 2^3S_1 or by collisions of the second kind with excited nitrogen atoms or molecules carrying electrons up from the 2^3P levels to the 2^3S_1.[11]

Conclusion

Lummer-Gehrcke spectrograms of the fine structure of the sharp series triplet taken under two conditions of optical excitation show striking differences and a fine structure different from that of the arc lines; establishing experimentally that the fine structure of a spectral line depends upon the method of optical excitation.

The writer wishes to express his sincere appreciation to Dr. A. Ellett who suggested the problem and who was a constant source of help and encouragement during the course of the investigation.

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August 11, 1928.

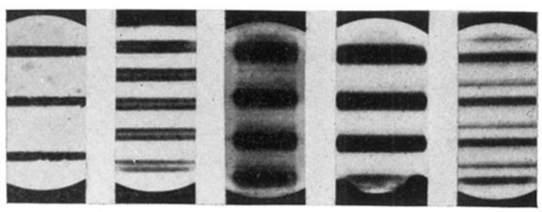

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Fig. 2. Enlargements of selected spectrograms.