THE ABSORPTION SPECTRA OF THE VAPORS OF ALUMINUM, GALLIUM, INDIUM AND THALLIUM IN THE ULTRAVIOLET

By John G. Frayne and Alpheus W. Smith

Abstract

(1) *Absorption in heated vapors.* The metals were vaporized in a graphite tube 15 cm long heated with an oxyacetylene torch to temperatures up to 2000°C. A tungsten under-water condensed spark provided a continuous spectrum. *Aluminum.* At about 1200°C the first 7 pairs of the first subordinate series were absorbed. The relative intensities differ from what might be expected from the Bohr theory standpoint. No absorption was observed for the second subordinate series. *Gallium.* At a temperature of about 1500°C, 17 prominent lines appeared, including the first 4 pairs of the first and second subordinate series and the 5th term of the $2p_1-ms$ series. *Indium.* At a temperature of about 1200°C, 18 lines appeared, including the first 3 pairs of the first subordinate series, the first 5 pairs of the second subordinate series and the 4th term of the $2p_1-md$ series. *Thallium.* At 400°C, 4 lines of the $2p_2-ms$ and 4 of the $2p_2-md$ series appeared, widening into bands with increasing temperature. At 800°C, lines from the $2p_1$ level appeared as fine absorption lines. These results verify those of Grotrian. (2) *Absorption in the arc.* A bead of the metal was placed in a crater. *Aluminum.* In a 15 amp. arc the lines of the $2p_2-md$ and $2p_1-md$ ($m=5$ to 11) were completely absorbed. *Indium.* Besides the resonance lines $2p_2-2s$ and $2p_2-3d$, the lines $2p_1-2s$ and $2p_2-3d$ were completely absorbed. (3) *Relative behavior of lines from $2p_1$ and $2p_2$ levels.* The lines for the $2p_1$ level for gallium and indium are as readily absorbed as those for the $2p_2$ level and therefore may also be resonance lines.

Introduction

INVESTIGATION of the absorption spectra of aluminum and thallium vapors has been made by McLennan, Young and Ireton.[1] Using the method of arc reversals they found band absorption corresponding to some of the higher members of the $2p_2-ms$ and $2p_2-md$ series. Their results will be discussed below. Grotrian[2] found the first pair of the first and second subordinate series in gallium vapor completely absorbed. In a previous paper[3] he tells of having found several members of the first and second subordinate series absorbed in the vapors of indium and thallium. He used the method of passing a continuous ultraviolet spectrum through the vapor of the metal in an evacuated quartz tube. He

[1] McLennan, Young and Ireton, Roy. Soc. Can. Proc., **13**, 9 (1919).
[2] Grotrian, Zeits. f. Physik **18**, 169 (1923).
[3] Grotrian, Zeits. f. Physik **12**, 218 (1922).

was limited to temperatures of 1200°C and found few lines below 2400A. In a recent paper Narayan, Gunnayya and Rao[4] found band and line absorption in thallium vapor corresponding to several arc lines, including 3776A ($2p_2-2s$). Guthrie[5] and later Wood and Guthrie[6] made investigations of absorption in thallium vapor. Uhler and Tanch[7] found the lines 4511A ($2p_1-2s$) and 4101A ($2p_2-2s$) absorbed in indium vapor.

The present investigation was undertaken with a view to extending Grotrian's work to aluminum. Further, since the method described below made it possible to use temperatures as high as 2000°C, it was thought that new information could be obtained for the vapors of gallium, indium and thallium. It was also thought that further study of absorption in this group might help put a more satisfactory construction on the real meaning of the $2p_1$ level. At the present time it is considered a metastable level, while the $2p_2$ level is chosen as the stable orbit. There is very little experimental evidence for such a distinction, as direct resonance measurements have only been reported on thallium. It is a well known fact that resonance lines are readily absorbed in the normal vapor of the element, but the elements of this group not only have their resonance lines but also lines from the $2p_1$ level appear as absorption lines. The difference $2p_2-2p_1$ is small for aluminum, about .10 volt, increasing to about .96 volt in thallium. It is true that Mohler and Ruark[8] found a resonance potential of .9 volt in thallium vapor and Jarvis[9] has found a similar potential of .3 volt in gallium vapor. Grotrian found that absorption of lines from the $2p_2$ level took place at a lower temperature than from the $2p_1$ level, the temperature difference increasing from about 100°C in gallium to about 400°C in thallium. However, the fact that he did find lines from the $2p_1$ level strongly absorbed, seemed to indicate that they might be placed in the same category as those from the $2p_2$ level.

Experimental Procedure

The metal under investigation was placed in a graphite tube 15 cm long open at both ends. An oxyacetylene torch was used as the source of heat. This method has been already described by Zumstein[10] who used it in a study of the absorption spectra of copper, silver and gold. In the

[4] Narayan, Gunnayya and Rao, Roy. Soc. Proc. **106,** 596 (1924).
[5] Guthrie, Dissertation (1908).
[6] Wood and Guthrie, Astrophys. J. **29,** 211 (1909).
[7] Uhler and Tanch, Astrophys. J. **55,** 291 (1922).
[8] Mohler and Ruark, J.O.S.A. **7,** 819 (1923).
[9] Paper not yet published.
[10] Zumstein, Phys. Rev. **25,** 523 (1925).

case of aluminum and thallium it was found necessary to pass a stream of nitrogen over the metal to prevent oxidation. At very high temperatures the aluminum combined with the nitrogen, making it difficult to secure sufficiently dense vapor to show absorption.

The continuous ultraviolet spectrum was produced by a condensed spark between tungsten electrodes under water. The spark circuit was similar to that described by Hulburt[11] with the exception that the auxiliary gap was an ordinary air gap with an air blast between the electrodes. This proved to be a very satisfactory arrangement, giving a continuous spectrum between 8000A and 2000A. A Féry type spectrograph was used throughout the work.

On account of the rapidity with which the graphite tube heated it was found impossible to take observations at temperatures which differed by less than 50°C.

Experimental Results

Aluminum. Several absorption lines appeared about 1200°C. They were found to correspond to well defined arc lines (see Table I). The first six pairs of the first subordinate series were absorbed, the absorption being more prominent in the shorter wave-lengths. The line 3092A ($2p_1-3d$) was more strongly absorbed than 3082A ($2p_2-3d$). Neither the lines 3962A ($2p_1-2s$) and 3944A ($2p_2-2s$) nor any other lines of the second subordinate series were absorbed.

Table I

Absorption spectrum of aluminum vapor

$\nu=2p_2-md$		$*\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
3	3082.16	3	3092.84
4	2567.997	4	2575.411
5	2367.064	5	2373.360
6	2263.453	6	2269.212
7	2204.627	7	2210.046
8	2168.805	8	2174.028
9	2145.390	9	2150.59
†10	2129.44	†10	2134.70
†11	2118.52	†11	2123.38

* New absorption lines.
† Absorbed in the arc.

The arc reversal method also was used to detect absorption. A small bead of the metal was placed in the crater of the positive carbon and vaporised in a 10 ampere arc. Some of the spectrograms showed complete

[11] Hulburt, Phys. Rev. **24,** 129 (1924).

absorption of five pairs of the first subordinate series, beginning with the fourth pair. In addition, narrow reversals were observed in the second and third pair as well as in the first pair of the second subordinate series. When a 15 ampere arc was used absorption was extended to the third pair of the first subordinate series.

Gallium. One gram of gallium gave sufficient vapor for absorption when heated to a temperature of about 1500°C. The first four lines of

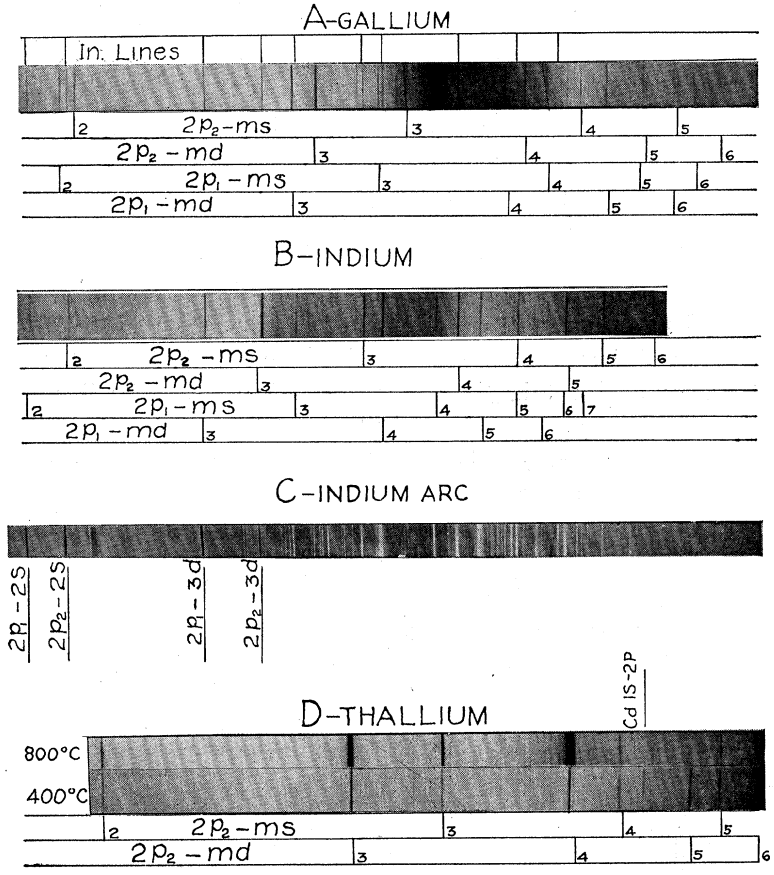

Plate I

the $2p_2 - ms$ and $2p_2 - md$ series were strongly absorbed. In addition, the first five lines of the $2p_1 - ms$ and $2p_1 - md$ series were absorbed. Band absorption occurred between 2620 and 2480A. This band became more pronounced at higher temperatures. The wave-lengths of the gallium lines given in Table II are taken from the Astrophysical Journal[6]

of May, 1922. Plate IA is a reproduction of one of the spectrograms taken with this vapor.

In addition to the gallium lines there appeared as impurities the indium lines $2p_2-ms$ ($m=2$ to 4), $2p_2-md$, ($m=3$ to 5), $2p_1-ms$ ($m=2$ and 3) and $2p_1-md$ ($m=2$ and 3).

TABLE II

Absorption spectrum of gallium vapor

$\nu=2p_2-ms$		$\nu=2p_2-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4032.975	3	2874.24
*3	2659.873	*4	2450.078
*4	2371.325	*5	2294.202
*5	2255.034	*6	2218.039
$\nu=2p_1-ms$		$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4172.06	3	2944.175
*3	2719.66	*4	2500.714
*4	2418.699	*5	2338.596
*5	2297.869	*6	2259.227
*6	2236.103		

* New absorption lines.

Indium. The lines absorbed in indium vapor are given in Table III. The first three lines of the $2p_2-ms$ and the first four of the $2p_2-md$ series

TABLE III

Absorption spectrum of indium vapor

$\nu=2p_2-ms$		$\nu=2p_2-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4101.764	3	3039.356
3	2753.889	4	2560.157
4	2460.079	5	2389.543
5	2340.191	12?	2181.70
*6	2278.20		
$\nu=2p_1-ms$		$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4511.38	3	3258.565
3	2932.633	4	2713.932
4	2601.756	5	2522.854
5	2468.12	6	2430.70
6	2399.25		

* New absorption lines.

were strongly absorbed. In addition the first five members of the $2p_1-ms$ and $2p_1-md$ series were absorbed. A line corresponding to the emission line 2181A was absorbed. This may be $2p_2-12s$ but as this leaves the

members of the series from $m=6$ to $m=11$ missing, the line is probably due to an impurity. All of the absorption lines occurred on every picture. Plate IB is a reproduction of a spectrogram taken at a temperature of about 1200°C. The emission spectrum of indium is reproduced in Plate IC. It will be noted that the lines $2p_2-2s$, $2p_1-2s$, $2p_2-3d$ and $2p_1-3d$ were completely absorbed in the arc. Aluminum emission lines were prominent in the arc but none appeared to be absorbed.

Thallium. Grotrian's observation that there was a 400°C difference between the appearance of lines from the $2p_1$ and $2p_2$ levels was verified in this investigation. The lines of the series $2p_2-ms$ ($m=2$ to 5) and $2p_2-md$ ($m=3$ to 6) appeared as fine absorption lines about 400°C. As the temperature increased these lines widened into bands extending asymmetrically toward the red. At 1200°C the lines $2p_2-2s$ and $2p_2-3d$ widened into bands of approximately 50A, while 2379A ($2p_2-4d$) extended about 38A. This latter line was the only one observed by Wood and Guthrie.[6]

TABLE IV

Absorption spectrum of thallium vapor

$\nu=2p_2-ms$		$\nu=2p_2-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	3775.72	3	2767.87
3	2580.14	4	2379.58
4	2315.93	5	2237.84
5	2207.06	*6	2168.61
$\nu=2p_1-ms$		$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	5350.46	3	3529.43 3519.24
3	3229.75	4	2921.52 2918.32
4	2826.16	5	2710.67
5	2665.57	6	2609.77
6	2585.59	7	2552.53
7	2538.18	8	2517.41
8	2507.94	9	2493.91
9	2487.48	10	2477.49
10	2472.57	11	2465.46
11	2461.93	12	2456.45
		13	2449.49
		14	2443.92
		15	2439.50
		16	2435.80
		17	2433.0

* New absorption lines.

At about 800°C the lines of the series $2p_1-ms$ and $2p_1-md$ appeared as fine absorption lines. These lines did not widen into bands as the tem-

perature was raised. The complete list of lines absorbed in this vapor is given in Table IV. Plate ID shows the lines from the $2p_2$ level only.

Discussion

The appearance of the aluminum lines is not what one would expect from the Bohr theory standpoint. In the first place, the resonance line 3944A ($2p_2-2s$) failed to appear as an absorption line. Secondly, the resonance line 3082A ($2p_2-3d$) appears only as a very faint absorption line, while the line 3092A ($2p_1-3d$) was much more prominent. Finally, the higher members of the series showed stronger absorption than those of longer wave-length. This latter point was also noted by McLennan, Young and Ireton,[1] who studied the absorption spectra by the arc reversal method. They found band absorption corresponding to lines of the $2p_2-ms$ ($m=4.5$ to 8.5) and $2p_2-md$ ($m=6$ to 14) series. They found no absorption of any lines from the $2p_1$ level.

The work of Grotrian[2] with gallium vapor was verified and thirteen new absorption lines discovered. He had found only the lines $2p_2-2s$, $2p_1-2s$, $2p_2-3d$, and $2p_1-3d$. The results of this investigation showed that lines from the $2p_1$ level were just as readily absorbed as those from the $2p_2$ level and that the term *resonance* might be equally applied to any line.

All of the lines found absorbed in indium vapor by Grotrian[3] were obtained on the spectrograms. In addition, the fifth member of the series $2p_2-ms$ (2278A) was strongly absorbed. The complete absorption of $2p_2-2s$, $2p_2-3d$, $2p_1-2s$ and $2p_1-3d$ points strongly to the suggestion that the latter pair might be considered in the same category as the former, which are recognised resonance lines. It is of interest to note that Uhler and Tanch[7] observed only 4511A ($2p_1-2s$) and 4101A ($2p_2-2s$) absorbed in indium vapor.

The results obtained in thallium vapor clearly differentiate between the $2p_2$ and $2p_1$ levels in this atom. The lines of the $2p_2-ms$ and $2p_2-md$ series appear without any of the lines of the $2p_1-ms$ or $2p_1-md$ series. Further, the lines from the $2p_2$ level are radically different from those from the $2p_1$ level in that they widen out into bands with increasing temperature whereas the latter lines remain as fine absorption lines. Only one new line 2168A ($2p_2-6d$) was found in this investigation. McLennan, Young and Ireton[1] found absorption bands in thallium vapor, corresponding to the lines $2p_2-md$ ($m=6$ to 10) and $2p_2-ms$ ($m=5.5$ to 11.5). They failed to find any absorption of lines from the $2p_1$ level. They explained their failure to find 3776A ($2p_2-2s$) by suggesting that the presence of Hg vapor was necessary to cause absorption

of this line. This investigation shows that temperature and density are the controlling factors in the production of lines in the absorption spectrum.

ANTIOCH COLLEGE,
YELLOW SPRINGS, O. (J.G.F.)

MENDENHALL LABORATORY OF PHYSICS,
OHIO STATE UNIVERSITY,
COLUMBUS, O. (A.W.S.)

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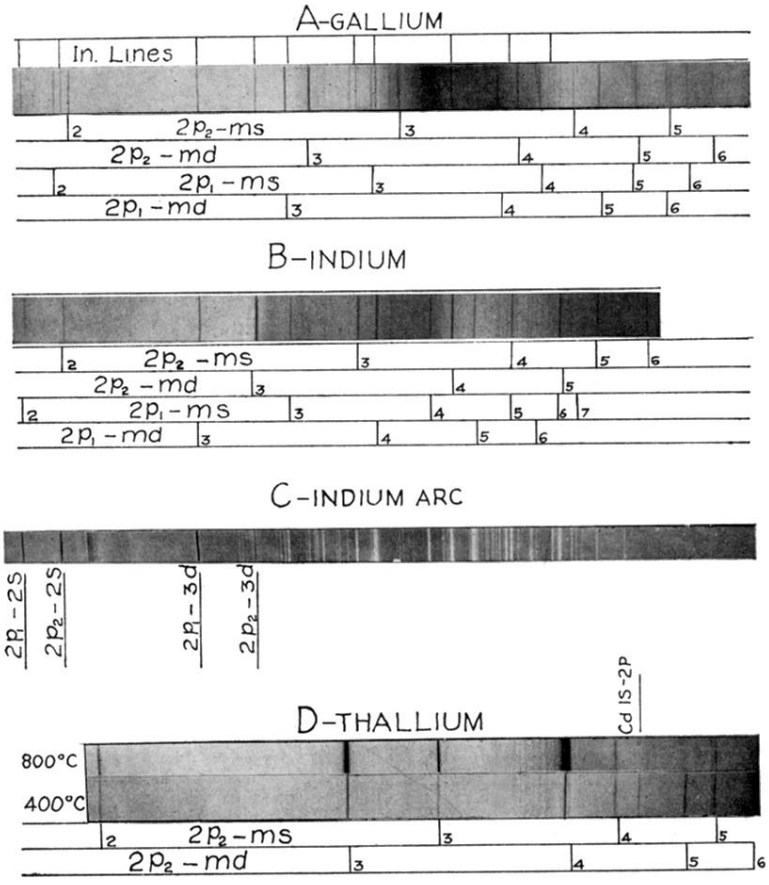
A-GALLIUM
In. Lines
2
2p2-ms
3
4
5
2p2 - md
3
4
5
6
2
2p1 - ms
3
4
5
6
2p1 - md
3
4
5
6
B-INDIUM
2
2p2 - ms
3
4
5
6
2p2 - md
3
4
5
2
2p1 - ms
3
4
5
6
7
2p1 - md
3
4
5
6
C-INDIUM ARC
2p1 - 2s
2p2 - 2s
2p1 - 3d
2p2 - 3d
Cd 1S-2P
D-THALLIUM
800°C
400°C
2
2p2 - ms
3
4
5
2p2 - md
3
4
5
6

Plate I