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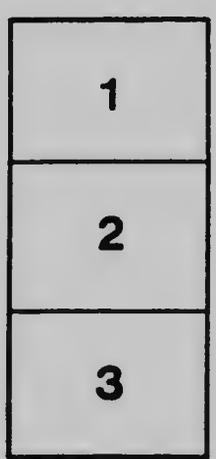

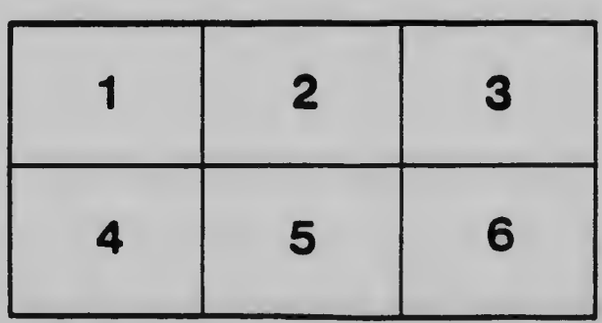

UNIVERSITY OF TORONTO STUDIES

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NOTES ON THE ABSORPTION SPECTRA OF THALLIUM, ALUMINUM, LEAD AND TIN, AND ARSENIC, BY J. C. MCLENNAN, E. F. BURTON, J. YOUNG AND H. J. C. IRETON

REPRINTED FROM THE PROCEEDINGS OF THE ROYAL SOCIETY OF CANADA, SERIES III, VOL. XIII

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On the Absorption Spectra of Thallium, Aluminium, Lead and Tin, and Arsenic

By PROFESSOR J. C. MCLENNAN, F.R.S., MR. J. F. T. YOUNG, M.A. and MR. H. J. C. IRETON, M.A.

(Read May Meeting, 1919.)

I. INTRODUCTION

Recent work by Foote, Rognley and Mohler[1] on the resonance and ionization potentials of thallium vapour by electrical methods gave the values 1·3 and 7·3 volts respectively for these magnitudes. In previous work by McLennan and others[2] it has been found that the resonance potential for certain elements is related by the quantum relation $ve = h\nu$ to the lowest frequency of the series $\nu = (1\cdot5\ S) - (m, p_2)$ and that the ionization potential is similarly given by applying the same relation to the limiting frequency of the series $\nu = (1\cdot5\ S) - (m, P)$. By analogy it was thought that the values of the potentials obtained for thallium could be used to determine these two series. The resonance voltage given above corresponds to radiation of wavelength 11, 513 A.U. which is a well known line in the infra-red while the ionization voltage gives the wavelength 1700 A.U. Reference to a recent paper by McLennan, Ainslie and Fuller[3] shows that no line had as yet been found with the frequency of the latter in the spectrum of thallium.

In a previous paper by two of the authors[4] the method of arc reversals was successfully applied in determining the series $\nu = (1\cdot5, S) - (m.P)$ for calcium strontium and barium. It was thought, therefore, that possibly further knowledge of the series of thallium and other metals might be obtained by an application of this method.

II. EXPERIMENTAL ARRANGEMENTS

A small Hilger quartz spectrograph Type A and Schumann plates prepared by the Adam Hilger Co., were used in taking the photographs of the spectra. The best results were obtained by focussing the light from the source on the slit with a cylindrical quartz lens. The arc arrangements were the same as that described in a previous paper.[5]

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[1] Foote, Rognley & Mohler, Phys. Rev. Vol. XIII, No. 1, Jan., 1919, p. 59.

[2] Guthrie Lecture by Prof. McLennan, Proc. Phys. Soc. London, Vol. I, pt. I, Dec. 15, 1918. Tate, Phys. Rev. Vol. X, No. 1, p. 81, 1917.

[3] Proc. Roy. Soc. Sec. A. Vol. 95, Mar. 15, 1919, p. 316.

[4] McLennan & Young, Proc. Roy. Soc. A. Vol. 95, 1919.

[5] McLennan & Young, loc. cit.

The arc was struck between blunt carbons, held at right angles, the vertical one being filled either with metallic salt or with the metal itself. Owing to the high melting point of the metals investigated it was found necessary to use currents of from 10–20 amperes at 200 volts. The vertical carbon was made positive and it was found that a few seconds after the arc struck metallic vapour was passing up in dense clouds in front of the arc which was maintained at the back edges of the carbon. The length of exposure varied from 30–60 seconds. Small supplies of vapour in the arc gave the emission spectrum only.

A calibration curve based on standard wavelengths in the spectra of mercury, zinc, cadmium and magnesium was employed to obtain the absorption wavelengths, measurements being taken for some known line as zero. A Hilger comparator was used in measuring the plates.

III. Absorption Spectrum of Thallium

Previous work by Guthrie[1] on the absorption spectrum of thallium has shown that pure thallium gives four absorption bands at 3230 A.U., 3092 A.U., 2330 A.U. and 2380 A.U. and on adding mercury additional bands appeared at 3776 A.U., 2768 A.U. and 2580 A.U. It was considered advisable to carry this work further into the ultra violet in the hope of obtaining absorption over a series of wavelengths.

With thallium the vertical carbon was filled with the chloride. In the heat of the arc the salt became dissociated and free metal was obtained in the form of vapour with a current of from 8–12 amperes at 200 volts.

The spectrograms showed absorptions at several places which agreed with those given by Dunz[2] for the series $\nu = (2,p_2)$—(m,d_t) and $\nu = (2,p_2) - (m,s)$.

These are: For series $\nu = (2,p_2) - (md')$

m =	6	7	8	9	10
λ =	2168·68	2129·39	2105·1	2088·2	2077·
m =	11	12	13	14	
λ =	2069	2062	2057	2053	
and for series $\nu = (2,p_2) - (m,s)$					
m =	5·5	6·5	7·5	8·5	
λ =	2152·18	2119·2	2098·5	2083	
m =	9·5	10·5	11·5		
λ =	2073	2065	2059		

[1] Guthrie Dissertation—Baltimore—1908.

[2] Dunz—Inaugural Dissertation—Tübingen—1911.

In addition to the above absorptions were recorded at 3230 A.U. and 2530 A.U., the latter line not yet assigned to any series. No absorption was found at 3776 A.U. which would indicate that the presence of mercury is necessary for this absorption. Two of the sixteen series lines have not previously been recorded. They are 2065 A.U. and 2059 A.U. belonging to the series $\nu = (2,p_2) - (m,s)$.

The reproduction in Plate I illustrates the nature of the absorption obtained with thallium vapour. Attempts were made to obtain absorption at 1700 A.U. with thallium salts in the carbon arc in vacuo with the fluorite spectrograph, but these have been up to the present unsuccessful. This may be due to the difficulty in producing dense enough vapours in vacuum arcs which were open to the pumps.

IV. Absorption Spectrum of Aluminium

In case of aluminium it was found impossible to use any of the salts owing to the formation of the oxide which was irreducible in the arc, so that the metal itself was used. No absorption was observed visually with a small glass spectroscope but the spectrograms revealed series of absorption bands in the ultra violet. When carefully measured it was found that the values agreed exactly with those given by Dunz[1] for the series $\nu = (2,p_2) - (m,d')$ and $\nu = (2,p_2) - (m,s)$.

In the former series nine absorption bands were found and in the latter, five. They were as follows:

Series $\nu = (2,p_2) - (m,d')$

m =	6	7	8	9	10
λ =	2263·83	2204·73	2169	2146	2130
m =	11	12	13	14	
λ =	2119	2111	2105	2100	

Series $\nu = (2,p_2) - (m,s)$

m =	4·5	5·5	6·5	7·5	8·5
λ =	2258·27	2199·71	2165	2141	2124

Since no other absorptions were observed, no new series relations can be predicted from the work, but it is of interest to note that the frequencies

$\nu = (2,p_2) - (12,d')$, $\nu = (2,p_2) - (13,d')$
$\nu = (2,p_2) - (14,d')$, $\nu = (2,p_2) - (6·5,s)$ and
$\nu = (2,p_2) - (7·5,s)$ have been recorded for the first time.

The reproduction shewn in Plate II is that of the absorption spectrum of aluminium.

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[1] Dunz, loc. cit.

V. Absorption Spectrum of Lead

Up to the present nothing has been known of the spectral series of lead. Hence it was thought the method of arc reversals spectra might throw light on the subject.

As in the case of aluminium the metal in granulated form, chemically pure, was used. Absorption bands were obtained fairly readily and extended down well into the ultra violet. It is interesting to note that absorption could be observed visually at $\lambda = 4058$ A.U.

In all, 19 reversals were obtained varying in type. It was found possible to classify them as follows:

Narrow Absorptions.	Diffuse Absorptions	Other Absorptions
4058 A.U.	2833 A.U.	2155 A.U.
2614 "	2400 "	2088 "
2247 "	2170 "	2054 "
2060 "	2015 "	2051 "
1973 "	1938 "	2049 "
1925 "	1911 "	2023 "
1900 "		

Since the absorption spectra of thallium and aluminium showed the same characteristics of narrow and diffuse absorptions it is possible that the series of narrow absorptions found in lead may correspond to that in thallium and aluminium, *viz.* $\nu = (2,p_2) - (m,s)$ and similarly the diffuse absorptions to the series $\nu = (2,p_2) - (m,d')$. Further work will be necessary to confirm this. The reproductions of Plate III show (*a*) the carbon arc spectrum, (*b*) the lead arc emission spectrum, (*c*) the lead arc absorption spectrum, and (*d*) that of the lead spark.

VI. Absorption Spectrum of Tin

The results obtained from the absorption spectrum of lead suggested similar work with tin for which nothing is known of spectral series. Unfortunately, the results were too meagre to make any prediction regarding series, since the only absorptions obtained were narrow reversals at 2141 A.U., 2096 A.U. and 2058 A.U. It is possible that these may belong to the same series but the other members have yet to be found.

The reproductions of Plate IV show (*a*) the spectrum of the carbon arc, (*b*) that of the tin emission arc, (*c*) that of the tin absorption arc, and (*d*) that of the tin spark in air.

VII. The Absorption and Flame Spectra of Arsenic

As a result of the extension of the work on electrical determination of resonance and ionizing potentials to the case of metallic

arsenic[1] it became of great interest to apply various methods of spectrum analysis to identify the predicted series. The resonance potential was found to be 4·7 volts and the ionisation potential 11·5 volts. These correspond to the emission of radiation of wave length $\lambda = 2620$ A.U. and $\lambda = 1070$ A.U. As has been pointed out already in the case of mercury, zinc, cadmium and magnesium, the absorption spectrum of the vapour and the Bunsen flame spectrum have been confined to the series $\nu = (1\cdot5,S) - (m,p_2)$ and $\nu = (1\cdot5,S) - (m,P)$ of which the first member of the former and last line of the latter are determined by applying the quantum relation to the resonance and ionising potentials respectively.

(*a*) *Absorption of Arsenic Vapour*

The same experimental arrangements were used as in the case of aluminium, thallium, tin and lead. Chemically pure metallic arsenic was vaporised from the vertical carbon of an ordinary rectangular arc with a current of 8–10 amperes. No visual absorption was observed but the spectrograms revealed strong unilateral band absorptions the sharp edges of the bands having the following wave lengths:

Head of band extending to approximately,

$\lambda = 2634\cdot5$ A.U.	$\lambda = 2624$ A.U.
2570·0 "	2550 "
2503·5 "	2483 "
2437·3 "	2418 "

The above are recorded as emission bands by Kayser.[2]

No line reversals were obtained in any part of the spectrum down to $\lambda = 1850$ A.U.

(*b*) *Flame Spectrum of Arsenic*

As will be observed the work on absorption spectra was in no way conclusive in determining the series which one would have expected from the work on resonance potential of arsenic vapour[3] to have its slowest frequency at about $\lambda = 2620$ A.U. In a further attempt to locate the series a study of the flame spectrum was undertaken.

The type of burner employed consisted of a steel annulus around the top of the tube of a Bunsen burner. The annulus was covered with a conical steel cover to direct the arsenic vapour into the Bunsen flame. This type of burner was previously successfully employed by

[1] Foote, Rognley & Mohler, Phys. Rev. Vol. XIII, Jan., 1919, p. 59.
[2] Kayser—Handbuch der Spectroscopie.
[3] Foote, Rognley and Mohler, *loc. cit.*

McLennan and Thomson.[1] The arsenic metal was placed in the steel annulus which was heated by a Bunsen burner; the vapour being driven into a gently burning flame.

Spectrograms were taken with a Hilger type A quartz spectrograph on Schumann plates prepared by the Adam Hilger Co. The exposures were of about seven hours' duration and the following arsenic radiation was recorded in addition to the ordinary Bunsen flame spectrum.

Lines at λ 3266 A.U., λ 2860 A.U., λ 2780 A.U., λ 2350 A.U. and λ 2288 A.U. and bands with heads at λ 2634 A.U., $\lambda = 2570$ A.U., $\lambda = 2503 \cdot 5$ A.U. and λ 2437·3 A.U., the weaker parts of the bands being towards the ultra violet.

A number of these correspond to flame lines found by Eder and Valenta.[2]

VIII. Summary

(*a*) *Thallium*

1. In addition to absorptions of thallium already discovered by Guthrie[3], further absorptions were obtained as arc reversals.

2. These additional absorptions in the ultra violet region were confined to the two series $\nu = (2,p_2) - (m,d')$ for values of $m = 6 - 14$ inclusive and $\nu = (2,p_2) - (m,s)$ for $m = 5 \cdot 5 - 11 \cdot 5$ inclusive.

3. The series $\nu = (2,p_2) - (m,s)$ has been observed for values of $m = 10 \cdot 5$ and $m = 11 \cdot 5$ for the first time.

4. No absorption was obtained in the region 1700 A.U. with the thallium arc in vacuo.

(*b*) *Aluminium*

1. The absorption spectrum of aluminium has been found to consist of fourteen bands in the extreme ultra violet.

2. As with thallium these absorptions are given by the series $\nu = (2,p_2) - (m,d')$ for values of $m = 6 - 14$ inclusive and $\nu = (2,p_2) - (m,s)$ for values of $m = 4 \cdot 5 - 8 \cdot 5$ inclusive.

3. The series $\nu = (2,p_2) - (m,d')$ has been verified for $m = 12$, 13 and 14 and the series $\nu = (2,p_2) - (m,s)$ for $m = 6 \cdot 5$ and $7 \cdot 5$ for the first time.

(*c*) *Lead*

1. In all, 19 absorption bands of lead were measured.

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[1] McLennan and Thomson. Proc. Roy. Soc. A. Vol. 92, 1916, p. 584.
[2] Eder and Valenta, Atlas, Typischer Spektren.
[3] Guthrie—*loc. cit.*

2. It is possible that the systems of narrow and diffuse absorptions may correspond to the analogous series absorptions of thallium and aluminium.

(*d*) *Tin*

1. Three absorption bands of tin were obtained but no identification of series is yet possible.

(*e*) *Arsenic*

1. The flame spectrum of metallic arsenic has been found to consist of five lines: $\lambda=3266$ A.U., $\lambda=2860$ A.U., $\lambda=2780$ A.U., $\lambda=2350$ A.U. and $\lambda=2288$ A.U. together with four bands with heads at $\lambda=2634\cdot5$ A.U., $\lambda=2570$ A.U., $\lambda=2503\cdot5$ A.U. and $\lambda=2437\cdot3$ A.U.

2. The arc absorption spectrum has been found to consist of four strong unilateral bands, the sharp edges of which were towards the red and occurred at wavelengths $\lambda=2634\cdot5$ A.U., $\lambda=2570\cdot0$ A.U., $\lambda=2503\cdot5$ A.U., $\lambda=2437\cdot31$ A.U.

3. Contrary to expectation no single line absorption or emission was found which could possibly be supposed to correspond to the line $\lambda=2620$ A.U. predicted by Foote and others.[1]

Admiralty Physical Laboratory,
South Kensington.

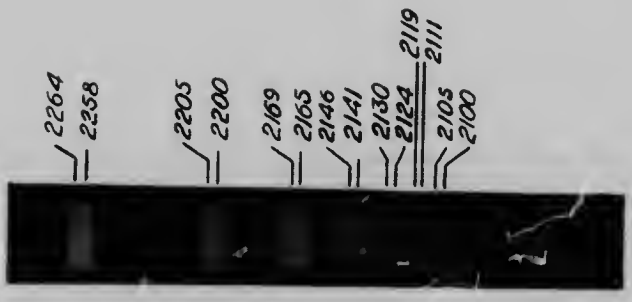
14th April, 1919.

[1] Foote, Rognley and Mohler—*loc. cit.*

PLATE I.

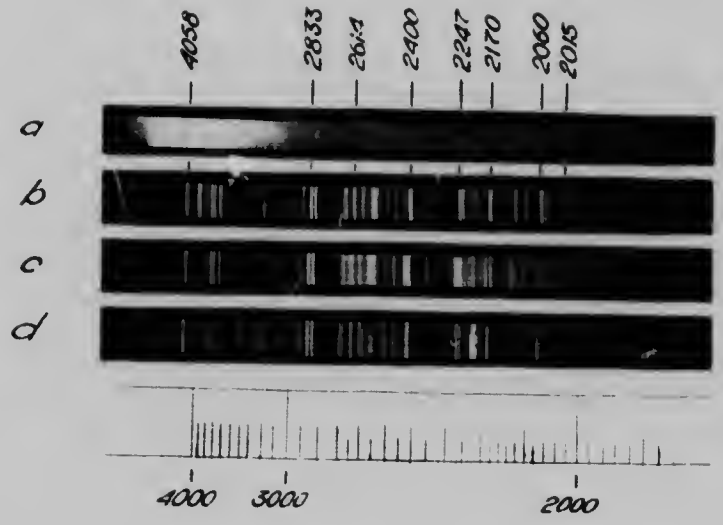
Thallium Absorption Spectrum.

PLATE II



Aluminium Absorption Spectrum.

PLATE III.



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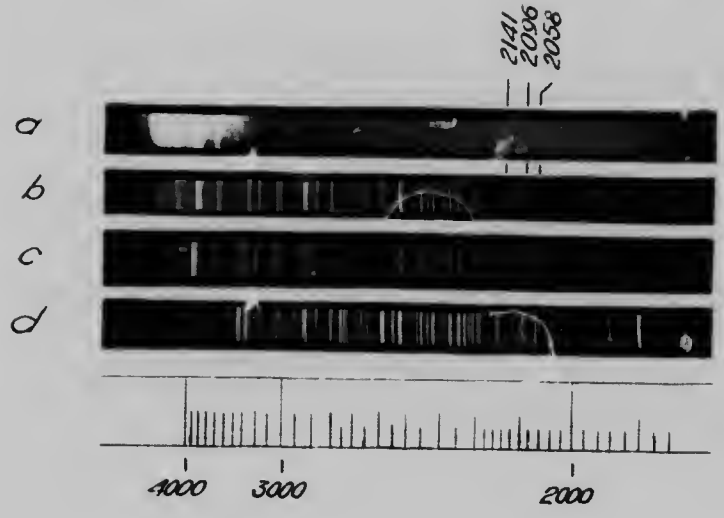

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