On the Bunsen Flame Spectra of Metallic Vapours.

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(Received July 17, 1916.)

[Plate 9.]

1. *Introduction.*

In seeking to solve the problem of the structure of atoms, especially of the more complex ones, it is of great importance to know what are the simplest or fundamental spectra which such atoms are capable of emitting. Information regarding such fundamental frequencies for the atoms of some metals has been obtained from investigating the characteristics of both the absorption and emission spectra of vapours of these metals. For example, McLennan and Edwards* have shown that, with the non-luminous vapours of mercury, zinc and cadmium, narrow absorption bands are obtained, using moderate vapour densities, with lines whose frequencies are given by $\nu = (1\cdot5, S)-(2, p_2)$,† and $\nu = (1\cdot5, S)-(2, P)$. The first of these is the frequency of the first member of Paschen's‡ combination series $\nu = (2, p_2)-(m, S)$, and the second is the first member of the singlet series $\nu = (1\cdot5, S)-(m, P)$. Moreover, one§ of us has also more recently shown from absorption experiments that for magnesium atoms the frequencies $\nu = (1\cdot5, S)-(2, P)$, $\nu = (1\cdot5, S)-(3, P)$, and possibly also those of still higher members of the series $\nu = (1\cdot5, S)-(m, P)$, are the fundamental ones. With this metal the frequency $\nu = (1\cdot5, S)-(2, p_2)$, does not appear from experimental evidence as yet available to be fundamental.

It has also been shown by McLennan and Henderson|| that the simplest spectrum which the vapours of mercury, zinc, and cadmium in a vacuum can be made to emit under bombardment by electrons consists with each of the metals of the single spectral line whose frequency is given by

* McLennan and Edwards, 'Phil. Mag.,' vol. 30, p. 695 (November, 1915).

† In the symbolic equation $\nu = (n, X)-(m, Y)$, the frequencies are given by $\nu = \dfrac{N}{[n+X+x(n, X)]^2} - \dfrac{N}{[m+Y+y(m, Y)]^2}$, where N is Rydberg's number, n has a fixed value, either integral or one of the numbers 1·5, 2·5, 3·5, etc., and m has successive integral values, each one giving the frequency of a member of the series.

‡ Paschen, 'Ann. der Phys.,' vol. 35, p. 860 (1911).

§ McLennan, *supra*, p. 574.

|| McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915).

$\nu = (1{\cdot}5, S) - (2, p_2)$. With magnesium, on the other hand, one of us* still later has shown that the simplest spectrum which can be obtained of magnesium vapour in a vacuum by means of electronic bombardment is given by $\nu = (1{\cdot}5, S) - (2, P)$. For mercury, zinc, and cadmium vapours, then, the frequency $\nu = (1{\cdot}5, S) - (2, p_2)$—and probably also $\nu = (1{\cdot}5, S) - (2, P)$—appears to be the fundamental one, while with magnesium it is in all probability $\nu = (1{\cdot}5, S) - (2, P)$.

As the electrical conditions in flames are probably simpler than those which obtain in the electric arc or spark, one should expect that, in flame spectra of the elements, the fundamental frequency would come out relatively with specially strong intensity. Charles de Watteville,† in a number of papers on flame spectra, has pointed out that, if a Bunsen flame be fed with the spray of salt solutions of a number of different elements, the spectrum of the flame with some of the elements consists of a single strong line, and with others of a single strong line accompanied by a number of very much fainter ones. These strong lines for the different metals, with their frequencies, are given in Table I.

Table I.

Element.	Frequency $\nu = 1{\cdot}5, S-2, p_2$.	Frequency $\nu = 1{\cdot}5, S-2, P$.
	Å.U.	Å.U.
Mercury	$\lambda = 2536{\cdot}72$	—
Zinc	$\lambda = 3075{\cdot}99$	—
Cadmium	$\lambda = 3260{\cdot}17$	—
Magnesium*	—	$\lambda = 2852{\cdot}22$
Calcium	—	$\lambda = 4226{\cdot}91$
Strontium	—	$\lambda = 4607{\cdot}52$
Barium	—	$\lambda = 5535{\cdot}69$

* Lorenser, 'Inaug. Diss.,' Tübingen, 1913.

This Table, it will be seen, emphasises the view that for mercury, zinc, and cadmium, the fundamental frequency is given by $\nu = (1{\cdot}5, S) - (2, p_2)$, while for magnesium, and probably also for calcium, strontium, and barium, it is given by $\nu = (1{\cdot}5, S) - (2, P)$. Some earlier experiments made by Gouy,‡ with salts sprayed into a flame, also confirm this view with respect to zinc and cadmium.

* McLennan, *supra*, p. 574.

† De Watteville, 'Phil. Trans.,' vol. 204, p. 139 (1904); and 'Comptes Rendus,' vol. 142 (1906).

‡ Gouy, 'Ann. de Chimie et Phys.,' vol. 18 (1879).

Observations have also been made by Hartley* and by Ramage† on the Bunsen and the oxy-hydrogen flame spectra of some nineteen of the elements. With mercury no characteristic lines were observed with either of these flames. With zinc, cadmium, and magnesium, spectra consisting of a number of lines came out with the oxy-hydrogen flame, but no characteristic spectra were obtained when the Bunsen flame was used. With calcium, strontium, and barium, however, the single spectral line whose frequency is given by $\nu=(1\cdot5, S)-(2, P)$, *i.e.* the fundamental frequency, came out strongly with the Bunsen flame, while the same line and several others in addition came out when the oxy-hydrogen flame was used. In the experiments of Hartley and of Ramage, the vapours of the pure metals as well as of the salts of these metals were used in studying the flame spectra. De Watteville‡ reports that he was unable to detect any characteristic line of the mercury spectrum in photographs taken of the spectrum of the flame of a Bunsen burner into which there was blown the spray from solutions of metallic mercury in nitric acid.

The only investigators who appear to have observed the line $\lambda = 4571\cdot38$ Å.U.—frequency $\nu = (1\cdot5, S)-(2, p_2)$—in the flame spectrum of magnesium are Liveing and Dewar,§ and Eder and Valenta.|| The former found in the spectrum of the light from magnesium burning in air a number of lines, among which those of the wave-lengths $\lambda = 4571\cdot38$ Å.U. and $\lambda = 2852\cdot22$ Å.U. came out with relatively strong intensity. The first-mentioned line they state was always narrow and sharply defined. Eder and Valenta in their experiments found that a Bunsen flame fed with magnesium emitted a spectrum consisting of the lines $\lambda = 5183\cdot79$, $5172\cdot87$, $5164\cdot49$, $4571\cdot38$, $3336\cdot82$, $3332\cdot33$, $3330\cdot04$, $3097\cdot00$, $3093\cdot09$, $3091\cdot11$, and $2852\cdot22$ Å.U., together with other lines which they attributed to magnesium oxide and to impurities in the magnesium. In their Atlas of typical spectra,¶ however, they give a spectrum of the flame from a magnesium-fed Bunsen burner which shows but the single line $\lambda = 4571\cdot38$ Å.U. of the magnesium spectrum.

As the Bunsen flame would appear to be the simplest possible means of exciting the fundamental frequencies in the atoms of easily volatilised metals the failure of Hartley, Ramage, and de Watteville to bring out these

* Hartley, 'Phil. Trans.,' A, vol. 185, p. 161 (1894); and 'Trans. Dublin Soc.,' N.S. vol. 7, Part XII, p. 341 (1901).

† Ramage, 'Roy. Soc. Proc.,' No. 459, vol. 70, p. 1 (1901).

‡ De Watteville, *loc. cit.*

§ Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 32, p. 189 (1881).

|| Eder and Valenta, 'Atlas Typischer Spektren,' and 'Beiträge zur Photochemie und Spektral-Analyse,' S. 411, 1904.

¶ Eder and Valenta, 'Atlas Typischer Spektren,' Tafel III, No. 1.

frequencies by means of this agency in the case of the metals mercury, zinc, cadmium, and magnesium seemed rather remarkable. It is not clear from the papers of Hartley and Ramage whether more than a casual examination was made of this point, but before accepting as final the conclusion which may be drawn from their results as to the probable impossibility of stimulating the fundamental frequencies of these elements by means of Bunsen flames, especially in regard to mercury, zinc, and cadmium it was thought desirable by the writers to subject this matter to a closer inquiry. This has now been done, with the result that it has been found possible to obtain with the Bunsen flame the fundamental frequencies mentioned of the spectra of mercury, cadmium, and magnesium, but up to the present it has not been found possible to obtain such with zinc.

2. *Apparatus.*

In the experiments two types of Bunsen burner were used. One, shown in fig. 1, consisted of an ordinary burner A, to which was attached at the top a steel close-fitting tubular cap BB, provided with a conical shaped cover C.

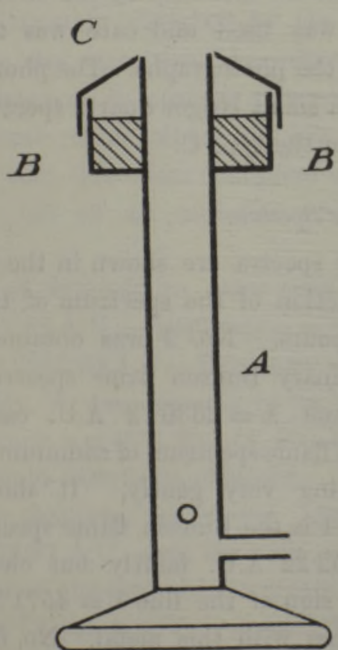


Fig. 1.

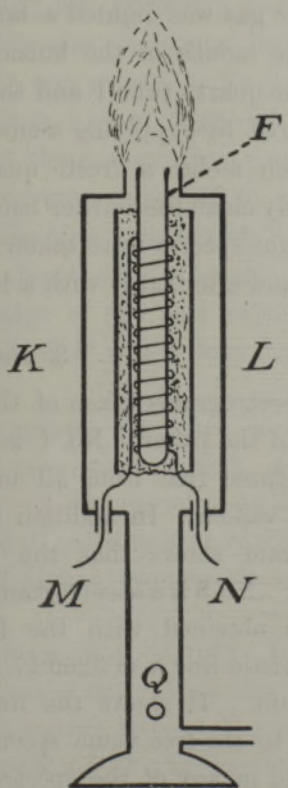


Fig. 2.

The metal to be vaporised was placed in the cup BB, and when the cover C was replaced and the burner lighted the flame of a blow-pipe was directed against the cup. The vaporised metal in escaping was thus made to pass directly into the flame of the burner.

The second form of burner used is shown in fig. 2. To the top of an ordinary Bunsen burner Q a brass cylinder KL, 3·8 cm. in diameter and 8 cm. high, was soldered. The top was closed by a lid containing an aperture in the centre 1·8 cm. in diameter, to which a small tube 0·5 cm. high was attached. Another brass cylinder, 2·8 cm. in diameter and 7 cm. in length, was supported in the centre and coaxially with KL by means of three asbestos plugs. This inner cylinder contained a quartz tube F, 1 cm. in diameter and about 8 cm. in length, drawn off to a neck about 0·5 cm. in diameter at the upper end. A coil of manganin wire MN was wound round this tube, and the ends were led out through two openings fitted with small porcelain plugs in the bottom of KL. A layer of asbestos paper was placed round the wire and then the whole space between the tube and the brass cylinder next to it was filled with plaster of Paris, which on solidifying kept everything rigid. The top of the quartz tube F came just level with the mouth of the burner. When the gas was lighted a large clear Bunsen flame was easily maintained above the mouth of the burner. The metals to be vaporised were placed within the quartz tube F and the furnace was raised to whatever temperature was desired by supplying a current of suitable intensity to the circuit MN. With each metal a fresh quartz tube was used and care was taken to thoroughly clean the burner before taking the photographs. The photographs of the flame spectra were taken first with a small Hilger quartz spectrograph, type A, and afterwards with a larger one of the type C.

3. *Bunsen Flame Spectra.*

The spectrograms taken of the different spectra are shown in the plate at the end of the paper. No. 1 is a reproduction of the spectrum of the clear Bunsen flame free from all metallic vapours. No. 2 was obtained with mercury vapour. In addition to the ordinary Bunsen flame spectrum this spectrogram shows that the mercury line $\lambda = 2536{\cdot}72$ Å.U. came out strongly. No. 3 is a spectrogram of Bunsen flame spectrum of cadmium vapour and was obtained with the flame burning very gently. It shows the characteristic line $\lambda = 3260{\cdot}17$ Å.U. No. 4 is the Bunsen flame spectrum of magnesium. It shows the line $\lambda = 2852{\cdot}22$ Å.U. faintly but clearly in addition to the free flame spectrum. No sign of the line $\lambda = 4571{\cdot}38$ Å.U. was found in any of the spectrograms taken with this metal. No. 5 is the spectrum obtained with thallium vapour. In this case the only characteristic

lines of the thallium spectrum which came out were $\lambda = 3775{\cdot}87$ Å.U. and $\lambda = 5350{\cdot}65$ Å.U. The former line was always much the stronger, but this may have been because the plates used were less sensitive to the green than to the ultra-violet. No. 6 is a. reproduction of the spark spectrum of cadmium, and No. 7 the Bunsen flame spectrum of cadmium vapour obtained when the draught was slightly forced and the flame was burning vigorously. As No. 7 shows that the line $\lambda = 2288{\cdot}79$ Å.U. came out faintly on the plates in addition to the line $\lambda = 3260{\cdot}17$ Å.U. under these circumstances. With zinc vapour no characteristic lines were obtained. Numerous modifications in the form of the burner were made and exposures were taken with them of varying duration, with the flame burning with different intensities, but in no case did the flame spectrum show any trace of the lines $\lambda = 3075{\cdot}99$ Å.U. and $\lambda = 2139{\cdot}3$ Å.U. or of any other of the zinc lines. Just why the zinc vapour failed to show any spectrum when results were obtained so easily with the other metals is not very clear.

4. *Discussion of Results.*

In view of the line $\lambda = 2288{\cdot}79$ Å.U. coming out in strong flames with cadmium vapour, it was thought that possibly the analogous line in the mercury spectrum $\lambda = 1849{\cdot}6$ Å.U. might come out as well. No trace of it, however, was found on any of the plates. It is known that both of these lines are strongly absorbed by the vapours of their respective metals, but, since the one came out, the other might have been expected to appear as well. However, it must be remembered that the line $\lambda = 1849{\cdot}6$ Å.U. is in the spectral region where the air begins to absorb very strongly, and it is possible that this effect combined with the action of the cool vapour in the flame to cut off all radiation of this wave-length which may have been emitted.

It is of interest to note that with magnesium no trace of the line $\lambda = 4571{\cdot}38$ Å.U.—frequency $\nu = (1{\cdot}5, \mathrm{S})-(2, p_2)$—was obtained. Since the line $\lambda = 2852{\cdot}22$ Å.U.—frequency $\nu = (1{\cdot}5, \mathrm{S})-(2, \mathrm{P})$—came out on the plates but feebly, it was scarcely to be expected that the line $\lambda = 2026{\cdot}46$ Å.U. —frequency $\nu = (1{\cdot}5, \mathrm{S})-(3, \mathrm{P})$—or others of higher frequency in the same series would have been obtained.

With thallium, as stated above, the lines $\lambda = 5350{\cdot}65$ Å.U. and $\lambda = 3775{\cdot}87$ Å.U. were the only ones which came out. They are the first members of the second subordinate doublet series given by $\nu = (2, p_1)-(m, s)$, and $\nu = (2, p_2)-(m, s)$, and are therefore analogous to the doublet yellow lines in the spectrum of sodium. The behaviour of thallium vapour in a

Bunsen flame, in so far as these experiments go, is exactly similar to the well known behaviour of sodium.

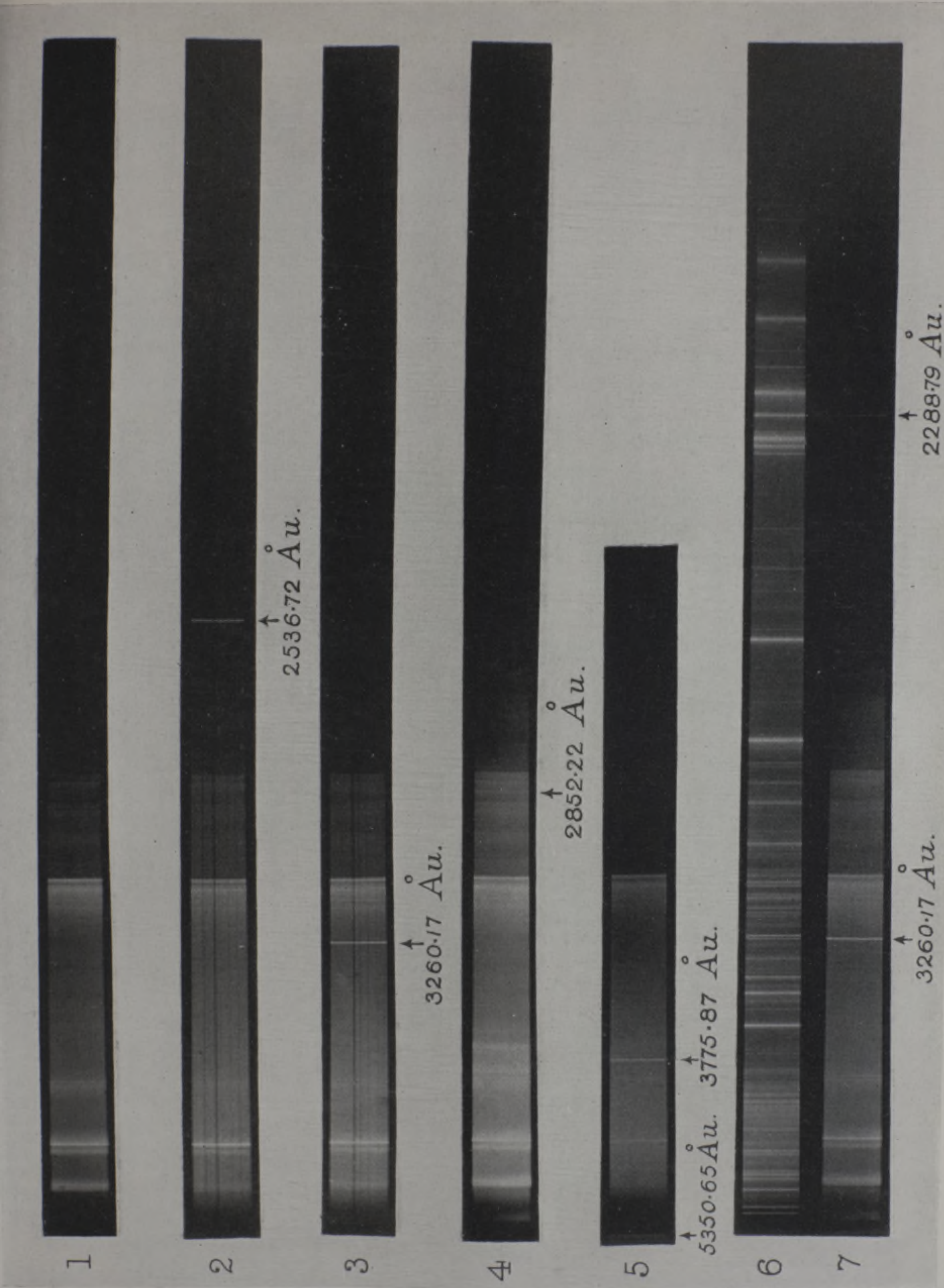
5. *Results.*

1. The results with mercury and cadmium vapours go to confirm the view that the frequency $\nu = (1{\cdot}5, S) - (2, p_2)$, is a fundamental one. The fact that the cadmium line $\lambda = 2288{\cdot}79$ Å.U. came out in strongly burning flames also gives support to the view that the frequency $\nu = (1{\cdot}5, S) - (2, P)$, possesses fundamental characteristics for cadmium atoms.

2. The experiments tend to support the view that, in the magnesium spectrum, the fundamental frequency is given by $\nu = (1{\cdot}5, S) - (2, P)$. It is the one most easily stimulated in the spectrum of magnesium. When the line $\lambda = 4571{\cdot}38$ Å.U. has been observed by other spectroscopists, it has always been accompanied by other lines, including in some cases that of wave-length $\lambda = 2852{\cdot}22$ Å.U.

3. The results obtained with thallium failed to give any indication of the fundamental frequencies in the spectrum of this element. It is probable that, with thallium, the fundamental spectral lines come far down in the ultra-violet region.

In conclusion, we wish to acknowledge the kind help of Mr. J. F. T. Young in taking some of the photographs.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