42(b) EXTENSION OF IRREGULAR DOUBLET LAW

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Recent work in this laboratory has shown that the irregular doublet law, first discovered in 1920 by G. Hertz in the X-ray region, and since then extended by Millikan and Bowen for the optical region is capable of much wider application. Millikan and Bowen have applied the law for the prediction and identification of spectra of atoms which are stripped to one or two valency electrons by vacuum discharge, and in the case of higher valence elements, for inner transition lines. But the law can be applied for the prediction of spectra of elements with a larger number of valency electrons giving rise to complicated spectra. The extension of the law in its most general form can be thus enunciated:

If we compare the spectra of a group of successive elements which are reduced by electric discharge to the same electronic constitution (for example, C, N^+, O^{++}, Fl^{+++}, N^{+4}), then frequencies of corresponding lines arising out of a transition in which the total quantum number remains unchanged will form an arithmetic progression.

The law can be very easily illustrated with the atomic chart given by one of the authors (*Phys. Zs.*, p. 470; 1927).

K_1
2

L_1 L_2
2 1

M_1 M_2 M_3
[1]⟶(1)⟶(1)

In this chart, horizontal transitions refer to $\Delta n=0$. Thus taking C, N^+, O^{++} ... we find that the origin of all possible groups of lines can be visualised as follows:

$$L_2L_2 \longrightarrow L_2M_1 \longrightarrow L_2M_2 \longrightarrow L_2M_3$$
$$(M_1 \longrightarrow M_2) \quad (M_2 \longrightarrow M_3)$$

Now the corresponding lines of the successive elements arising out of the transitions

$L_2M_1 \longrightarrow L_2M_2$, that is, $({}^3P, {}^1P) - \begin{pmatrix} {}^3D, & {}^3\bar{P}, & {}^2S \\ {}^1D, & {}^1\bar{P}, & {}^1S \end{pmatrix}$ lines,

and

$L_2M_2 \longrightarrow L_2M_3$, that is, $\begin{pmatrix} {}^3D, & {}^3\bar{P}, & {}^3S \\ {}^1D, & {}^1\bar{P}, & {}^1S \end{pmatrix} - \begin{pmatrix} {}^3F & {}^3\bar{D} & {}^3P \\ {}^1F & {}^1\bar{D} & {}^1P \end{pmatrix}$

will form arithmetic progressions.

Application of this law can be extended to all other complicated spectra.

It follows that if the spectra of two elements, preferably successive, of any group be known, it becomes quite easy to predict the spectra of the remaining elements.

In the group just mentioned, namely, C, N^+, O^{++} ...the spectra of N^+ has been completely elucidated by Fowler and Freeman, and that of O^{++}, is nearing completion thanks to the work of Mihul. (Mihul's levels are wrongly given, though his multiplets are correct. They can be easily reshuffled and correctly fitted to Hund's theory.) We can then predict the spectra of C, which is still unknown. Then $L_2(M_1 \longrightarrow M_2)$, as well as $L_2(M_2 - M_3)$ lines which are next in intensity to the fundamental $L_2L_2 \longrightarrow L_2M_1$ $({}^3P, {}^1\bar{D}\ {}^1S) - ({}^3\bar{P}, {}^1\bar{P})$ lines are found to be beyond 8000 A.

In a similar way, spectra of all groups can be predicted and correctly located.

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43. THE ORIGIN OF NEBULIUM SPECTRUM

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In a letter to Nature of Oct. 1, 1927, p. 473, Mr. Bowen has announced the very interesting relationship that some of the lines of unknown origin which are found in the nebulae and in the Wolf-Rayet stars and were so long attributed to a hypothetical element nebulium, are really due to ionised light elements like O^{++}, N^{++}, O^+, N^+ ...; they do not arise from the transitions usually allowed, but are due to transitions which are usually prohibited.

Prof. A. Fowler has also lent his support to this hypothesis. The object of this note is to discuss the nature of these transitions.

Mr. Bowen finds that the following well-known trio of nebulium lines are due to O^{++}, and due to transitions shown below:

5006·84	$^3P_2$—$^1\bar{D}_2$
4958·91	$^3P_1$—$^1\bar{D}_2$
4363·21	$^3P_1$—$^1\bar{S}_0$

The structure diagram of O^{++} is shown below:

O^{++} ... $2K$ $2L_1$ L_2

$M_1 \longrightarrow M_2 \longrightarrow M_3$

$2L_2(p^2)$ gives us $^3P_{0\,1\,2}$, $^1\bar{D}_2$, $^1\bar{S}_0$.

All other four-valence elements, namely, C, N^+, O^{++}, ... and C, Si, Ge, Sn, Pb have similar ground levels due to the electron-configuration p^2, that is, two electrons in p- (or L) orbits. The lines arise from transitions between metastable levels as pointed out by Bowen. It is interesting to note that though such transitions are not found in the spectra of light elements, they are of frequent occurrence in the spectra of heavy elements. In the spectrum of Pb, which is analogous to that of O^{++}, the values of the fundamental levels are

$^3P_0$	$^3P_1$	$^3P_2$	$^1\bar{D}_2$	$^1\bar{S}_0$
59821	52004	49173	38365	30355

Dr. Sur (*Phil. Mag.*, vol. 2, p. 623; 1926) in this laboratory found that the following lines exactly analogous to the above-mentioned nebulium lines are obtained in the heavy arc of lead. They are not present in the usual arc:

$^3P_1$—$^1\bar{D}_2 = \nu 13637$, $\lambda = 7330$ A.

$^3P_1$—$^1\bar{S}_0 = \nu 21649$, $\lambda = 4618$ A.

Other elements of the same group, namely, C, Si, Ge, Sn, can theoretically give similar lines, as the following Table shows, but a scrutiny of the existing literature shows that they have not yet been obtained. Whether they can be obtained in the heavy arc is yet to be seen.

$^3P_1$—$^1\bar{S}_0$ for	C	?
	Si	$\nu 15317$
	Ge	$\nu 15810$
	Sn	$\nu 19101$

Let us now consider the nature of violation of the selection principle. I have shown that in the case of complex spectra the selection principle can best be explained not in terms of the different quantum numbers, but in terms of *electron transition*. Thus $pp \rightarrow ps$ or $pp \rightarrow pd$ transitions are allowed (one electron changing from the p-orbit to the s-orbit, or the d-orbit, corresponding to $\triangle k = \pm 1$ where k=azimuthal quantum number), but $pp \rightarrow pp$ transitions are not allowed ($\triangle k = 0$). In terms of the structure diagram, this means that only those transitions are allowed in which the total number of electron transition is odd. Hence the transition involved in the origin of the nebulium lines really violates the selection principle $\triangle k = \pm 1$; we have here $\triangle k = 0$, and in addition $\triangle n = 0$ (change of total quantum number $n = 0$).

It is well known from the experiments of Koch on helium and other subsequent experiments, as well as from theoretical considerations, that such violations take place when the region where the spectrum is produced is traversed by a big electric field, or in regions where the free charge density is high. In heavy elements, the principle is easily violated, because the central atomic field deviates largely from the radial. A big external electric field, or free electric charges, would help the process, where such internal fields are not present, as in light elements, or are insufficient. Such, in fact, is the interpretation to be put on Dr. Sur's results. Similarly, in other heavy elements, namely, Bi, Th, Au, prohibited transitions of this type are very frequent.

Bowen's interpretation of the nebulium lines as being due to prohibited transitions in light elements therefore implies that unusually big electric fields are present in nebulae and Wolf-Rayet stars. This can be explained, because, owing to the extremely high temperature, matter must be in a very highly ionised state, and large fluctuations of electrical density, owing to accumulation of charges of one sign, must be very frequent. Bowen further finds that besides these lines, lines due to the transitions L_2M_1—L_2M_2 and $L_2M_2 \rightarrow L_2M_3$ of O^{++} are obtained in these stars. The fact that the electron, while returning from the higher excited group of orbits (due to L_2M_2), appears to linger too long in the less stable $^1D_2$ of the L_2L_2 combination, is to be attributed to this big electric field.

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