The Origin of Optical Spectra.

AMONG the many remarkable communications made this year to Section A (Mathematics and Physics) of the British Association, which, grouped together, will probably mark it off as an outstanding meeting, the address by the sectional president, Prof. McLennan, on the origin of spectra, was not the least interesting. From among the many subjects he surveyed it may be of interest to select some, and to try to give a not too technical account of these, showing the sort of progress that is now being made under the stimulus of Prof. Bohr's theory.

We agree now that all spectra are emitted by atoms or molecules during the process of return to their normal state after a more or less violent disturbance, and that any particular spectrum is emitted only by a particular atom or molecule after a suitable disturbance. We agree too (partly for theoretical, partly for experimental reasons) that spectra can be divided into two distinct types—line spectra or series spectra and band spectra or many-line spectra—which have their origin in the reconstruction of atoms and molecules respectively. It is with recent advances in the more advanced and more important study of these atomic or line or series spectra, emitted during the reconstruction of atoms, that the president dealt, and with these only shall we be concerned here.

Physicists will agree that an atom consists of a very small massive nucleus of positive electric charge Z units, the unit being the charge on the electron, surrounded by a planetary system of Z electrons. These move, when undisturbed, as a conservative system in a set of orbits which must have a definite structure, controlled by laws of which we are not yet masters, to which, however, the present quantum theory gives the most complete expression yet achieved. The number Z is called the atomic number of the atom, and specifies its place in the periodic table and all its physical and chemical properties. We can agree further that the orbits of the Z electrons are not all essentially different. They can be classified in groups, orbits of which are characterised by the same values of certain integers (three to each orbit), commonly called quantum numbers.

There are a variety of disturbances to which such an atom can be subjected. By suitable means supplying sufficient energy we can shift one or more of its electrons from their normal orbits, either right out of the atom, or into other possible orbits characterised by different quantum numbers. In the subsequent reconstruction the atom will emit a spectrum of sharp lines of definite frequencies characteristic of itself and the particular disturbance it has suffered. Each separate line is emitted during the return of an electron from one particular permissible orbit to another of less energy, and its frequency is related to these orbital energies by the most fundamental equation of the quantum theory $E_1 - E_2 = h\nu$. After the partial removal of a particular electron we merely get part of the spectrum corresponding to complete removal of the same electron. We can therefore, speaking generally, classify the complete line spectrum of a given atom into a number of separate spectra, each of which is associated with the recapture of one electron

by an atom after the removal of any specified set of its original Z electrons. Classified thus, an atom's spectra will divide into two well-marked types—those in which one or more of its deeper lying electrons have been removed and those in which the electrons removed, whatever their number, are entirely those most lightly bound. In the first type we can and do find internal reorganisations taking place before a new electron is captured. These are the X-ray spectra, with which we are not here concerned. In the second type no such reconstruction can occur, except while the new electron is being brought in. These spectra, which theoretically must all be of the same general series type, are called the optical spectra of the atom.

The typical optical spectrum (the so-called arc spectrum) of an atom is agreed to be that which is emitted during the return of the last (Z th) electron to an atom in which the rest of the system is in its normal state. When such a spectrum is fully analysed it is found that the lines can be arranged in series which display a certain fundamental constant R , Rydberg's constant. The value of this constant and its perpetual occurrence in all arc spectra is (as is well known) properly predicted by the theory. But this is not all. If we call the ordinary arc spectrum $Z(I)$ and its Rydberg's constant R , the theory we have outlined predicts Z optical spectra in all, of which the Q th spectrum $Z(Q)$, with constant Q^2R , will be emitted by the atom with its first ($Z-Q$) electrons in their proper orbits as it catches its $(Z-Q+1)$ th electron. The characteristic frequencies of these spectra will, of course, get higher and higher as Q increases, and for the later "optical" spectra of a heavy element will lie in the X-ray region. It is not the frequency range but the type of spectrum which remains characteristically optical.

The predicted second optical spectra $Z(II)$, with Rydberg constant $4R$, have been known for some years for a number of elements, under the general name of spark spectra; until recently we have had no experimental confirmation for values of Q greater than 2. In the last year there has been a great advance, for the third optical spectrum of aluminium with constant $9R$ has been obtained by Prof. Paschen, and the fourth and parts of the third optical spectra of silicon with constants $16R$ and $9R$ respectively by Prof. Fowler. These spectra are known by the very convenient notation of $AlIII$, $SiIV$ and $SiIII$. It will be seen that the spectra $SiIV$, $AlIII$, $MgII$ and NaI are all concerned with the capture of the eleventh electron by an atom (of varying Z) which has already bound its first ten electrons in their permanent orbits. These four spectra should be and are of the greatest similarity in their finer details. Their further detailed comparative study should be fruitful.

Prof. McLennan also pointed out that this successful study should throw light on the various optical spectra of the analogous series of elements, lithium, beryllium, boron, and carbon. In this difficult and very important region little progress has hitherto been made, but Prof. McLennan seemed hopeful that, with the theoretical and comparative guides now available, a renewed

attack would be successful in completing and classifying these spectra.

These are the broad outlines; let us now turn to finer details. It is well known that the theory, though it gives us general information about all optical spectra, so far can only predict in all its finer details the spectrum due to the binding of the first electron. The only spectra of this type yet experimentally realised are what we may now call H I and He II, that is, the spectrum of atomic hydrogen of which the most conspicuous feature is the well-known Balmer Series, and the spectrum of ionised helium. Now the predictions of the theory not only give the exact position of each line, but, as is well known, also assign to each line a definite complex structure. Under very high dispersion and first-class conditions this structure can be observed. In the case of He II, where the separations are greater and the conditions less severe, the confirmation of the theory was completed some years ago by the photographs of Prof. Paschen and others. Until recently, however, the similar more difficult experiments for the Balmer Series have been inconclusive and discordant. For this series the theory demands that each line should split into two close lines of the same frequency difference, which should themselves have a still finer detailed structure. Into this we need not enter, beyond saying that this ultimate structure should slightly reduce the apparent separation of the lines of longest wave-length, particularly H_α. Now the last lacuna has been filled by a brilliant piece of work in Prof. McLennan's laboratory, for good photographs have been obtained showing clearly the main separations of the five lines of longest wave-length. The agreement with the theory is complete. To illustrate the fineness of the detail it may be mentioned for example that for the fourth line H_δ, wave-length 4101.73×10^{-8} cm., the theoretical main separation is only 6.1×10^{-10} cm.

It has been known for some time that the energy required to remove one electron from neutral helium was (in the usual terminology) about 25 volts. We thus express the energy acquired by an electron in falling freely through such a potential difference. Thus expressed the energy required to remove the most lightly bound electron is known as the ionisation potential. Until recently the known part of the spectrum He I made no allowance for a normal atom in which the electrons were so firmly held. It appeared that these ought to be a series of lines in the far ultra-violet, not hitherto observed, associated with the reconstruction of the normal atom. Four such lines have now been observed by Lyman. The wave-lengths are very short, from 500 to 600×10^{-8} cm., and indicate an ionisation potential of 24.5 volts, in good agreement with direct observation. Our experimental knowledge of He I is thus properly rounded off. Much valuable work on the theory of this spectrum has also been completed, but the results are negative. It is now certain that none of the models so far proposed possess the proper permissible orbits, computed according to the rules of the present quantum theory, to account for the spectrum He I and the ionisation potential. It is an advance to be sure of this. The interaction of the two electrons in helium (and *a fortiori* the Z electrons in the general atom) must be

even more subtle, and the *detailed* theory of their orbits must lie even deeper, than has been hoped hitherto.

Recent work has shown the very great value of the study of the absorption spectra of atomic vapours in the coldest state in which they can be procured at reasonable densities. Such vapours, as is well known, absorb selectively a number of sharp lines which are a selection of the lines of the first optical (emission) spectrum. But since the atoms of the vapour must in general be in their normal state, only those lines can appear which belong to atomic reconstructions ending in this normal state. We can thus select from the whole mass of lines just those associated with one particular state of the atom, and that the most important. In this way certain difficulties have been cleared up in connexion with the spectrum Al I and its analogues. It had been believed that the normal orbit of the most lightly bound electron was of the same type for all atoms—that is, specified by a certain value (unity) of one of its quantum numbers. This is the theoretical interpretation of the empirical belief that the absorption spectrum would always consist of the same type of series. But the known facts about this group of spectra did not fit in with this belief, and it is now definitely established by the study of absorption spectra that this belief is false. The normal orbit in question may have at any rate one or two for the value of this quantum number, and has the value two for aluminium and its analogues. Thanks to this we now know that our account of these spectra is reasonably complete. The study of absorption spectra will doubtless prove of great value in disentangling the difficult spectra of the lead-tin group. A good start has recently been made in their classification.

Let us with Prof. McLennan conclude by referring to the effect of an applied magnetic field on the atomic orbits, with which is bound up the question of the way in which the atom orientates itself in space under such an influence. The effect on the spectrum is known as the Zeeman effect, and its study is proving of the utmost importance to the theory of atomic structure. It is here that we shall probably win the next advance. We can scarcely expound these questions shortly and cannot enter into details here. But it may be said that the proper classification of the empirical facts, largely the work of Prof. Lande, seems already fairly complete, and that their theoretical interpretation has been begun on a sure basis. We must not, however, omit to mention the cognate beautiful experiment of Stern and Gerlach, which consists in directing atoms of silver of known velocity through a strong non-uniform magnetic field. If the atom possesses a magnetic moment it must be deflected, unless its axis is always perpendicular to the field. Such deflexions were observed, and appear to prove, simply and directly, that the normal free atom of silver possesses a definite magnetic moment and always sets itself with its magnetic axis parallel or anti-parallel to the field. Experiments such as these are of the greatest importance. They admit of unambiguous interpretations and provide the necessary strong points from which the attack on the complicated Zeeman effect and related phenomena can be securely launched.

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