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THE SERIES SPECTRA OF TWO-VALENCE-ELECTRON ATOMS OF PHOSPHORUS (P_{IV}), SULPHUR (S_V), AND CHLORINE (Cl_{VI})

By I. S. Bowen and R. A. Millikan

Abstract

Series spectra of two-valence-electron atoms of P, S, and Cl.—In a previous paper,[1] the regular and irregular x-ray doublet laws were used to predict the spectra of stripped atoms, that is, atoms having only one valence electron. The method has now been applied to the spectra of two-electron atoms, since, although these spectra consist of triplets or singlets instead of doublets, the same laws apply to them. In this way 23 lines of P_{IV} have been identified, 17 lines of S_V and 6 lines of Cl_{VI}. With the help of the Ritz equation, 12 term values of P_{IV} and 8 of S_V were also determined. In a table are collected all known term values for two-electron atoms of Mg, Al, Si, P and S.

Physical significance of the x-ray irregular doublet law.—Spectral lines which give parallel curves on a Moseley diagram $\sqrt{\nu/R}$ plotted as a function of atomic number) and which therefore follow this law, are produced by jumps between orbits of the same total quantum number but with different screening constants.

I. Introduction

THE present paper is merely a further illustration of the fecundity of the method for the identification of spectral lines which we have recently brought to light. This method grows out of the discovery that both the regular and the irregular x-ray doublet laws are also applicable throughout the whole field of optics[1] so long as a series of atoms of like electronic structure but varying effective nuclear charge is under observation. The irregular doublet law makes possible the prediction of the precise position of a particular line, while the regular doublet law foretells the character of its fine structure, i.e. the frequency separation of its components.

We have heretofore used the irregular doublet law only to predict the positions of lines belonging to a stripped-atom series, i.e. the series constituted by the stripped atoms of Li, Be, B, C, N, or of Na, Mg, Al,

[1] Bowen and Millikan Phys. Rev. **24**, 209 (1924)

THE ABSORPTION COEFFICIENT FOR SLOW ELECTRONS IN GASES

By Robert B. Brode

Abstract

Electrons from a heated filament were accelerated through a slit and deflected magnetically around a circular path into a Faraday cylinder connected to a galvanometer. From the plots of the logarithm of the ratio of the galvanometer current G to the total electron current M from the filament, as a function of the pressure, the absorption coefficients were determined for various accelerating voltages from 2 to 360. For a given voltage, the absorption coefficient was found to be independent of the current M and also of the pressure (at about 10^{-2} mm). The results of Mayer and Ramsauer were checked for *argon* and *helium*. In argon, the coefficient reaches a sharp maximum at about 12 volts, the value for 2 volts being only one-fifth of the maximum value. In helium there is a maximum at 4 volts. *Methane* gave a curve similar to these, with a maximum at about 7.5 volts, which is in agreement with the results of Akesson. The curves for *nitrogen* and *carbon monoxide* are nearly identical, both having a maximum at about 18 volts and a minimum at about 9 volts. The curve for *hydrogen* shows no maximum, the coefficient increasing steadily down to 2 volts.

THE absorption of electrons in gases is due to the formation of negative ions and to the reflection from molecules. The electron is considered as absorbed when it disappears from the original beam by a change of its direction of motion or by loss of energy. The dependence of this absorption on the velocity of the electrons was first investigated by Lenard.[1] With an apparatus similar to that used by Lenard, Niels Akesson[2] found that the absorption in methane was a maximum at 8 volts, and that the slower electrons were much less absorbed. He found no selective absorption in hydrogen. The other gases which he investigated, CO, CO_2, C_3H_6, N_2O, N_2, and O_2 all indicated two maxima in their absorption curves.

The absorption coefficient for slow electrons in gases has been measured by C. Ramsauer[3] and H. F. Mayer.[4] These observers found that the absorption coefficients for hydrogen, nitrogen, helium and neon remained nearly constant, usually decreasing a little as the velocity of the electrons was increased. For argon they found that the absorption coefficient had

[1] P. Lenard, Ann. der Phys. **12,** 714 (1903)
[2] Neils Akesson, Lund's Acta N. S., 2, **12,** No. 11 (1916).
[3] C. Ramsauer, Ann. der Phys. **64,** 513 (1921).
[4] H. F. Mayer, Ann. der Phys. **64,** 451 (1921).

a maximum value at 13 volts. As the voltage was decreased below 13 volts, the value of the absorption coefficient decreased steadily until at 0.7 volt, their lowest observation, it was 1/30th of its maximum value. With increasing voltage above 13 volts the absorption coefficient steadily decreased.

Minkowski and Spooner[5] predicted from an experiment on the effect of gas on the space charge about a hot filament, that krypton and xenon should show this same phenomenon. Subsequent observations by Ramsauer[6] verified their prediction. The maxima in these gases were even more pronounced than in argon. G. Hertz,[7] by a method similar to that used by Mayer, confirmed the variation of the absorption coefficient in argon with changes of the velocity of the electrons. Townsend and Bailey[8] obtained data from the diffusion of electrons through argon that indicated very small values of the absorption coefficient for slow speed electrons.

The method used by Ramsauer to obtain a beam of uniform velocity electrons was used in this investigation. A series of slits were arranged on a circle and some of the electron paths were bent into this circle by a magnetic field. The radius of the circle in which a uniformly moving electron moves due to a magnetic field is given by the equation, $H \cdot r = 3.3\sqrt{V}$, where H is the magnetic field strength in gauss, V the energy of the electron in equivalent volts and r the radius of the path in centimeters. By making the slits narrow in comparison with the radius of the circle a beam of electrons could be obtained with practically uniform velocity.

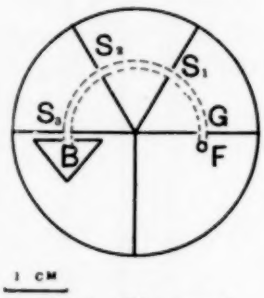


Fig. 1. Diagram of apparatus.

Apparatus

The apparatus used is shown in Fig. 1. It was made of copper parts silver-soldered together. The source of electrons was the filament F, a helix of tungsten wire usually operated at about 1.2 amp. The potential drop across the filament was then about 4 volts. The current for the filament was supplied by a storage battery maintained at a negative potential with respect to ground. The filament was placed 1 mm from the grid G which contained 10 holes 1 mm in diameter. The slits S_1, S_2

[5] Minkowski and Spooner, Zeits. f. Phys. **15**, 399 (1923)
[6] C. Ramsauer, Jahrb. Rad. u. Elek. **19**, 345 (1923)
[7] G. Hertz, Proc. Amsterdam Acad. **25**, 80 (1922)
[8] Townsend and Bailey, Phil. Mag. **44**, 1033 (1922).

and S_3 were rectangular, 1 mm wide and 1 cm high, and placed with their centers on a circle 1 cm in radius. The slits, grid and enclosing box were soldered together and connected to ground. A micro-ammeter measured the total emission of the filament and this reading, M, was taken as proportional to the electron stream that started around through the slits. The electrons that reached the box B went to ground through a galvanometer G, which measured the electron stream at the end of the path. The length of the path was 3.2 cm. The magnetic field that bent the electron stream into the circular path was produced by a solenoid 15 cm in diameter and 30 cm long, in which a current of 1 ampere produced a field of 19 gauss.

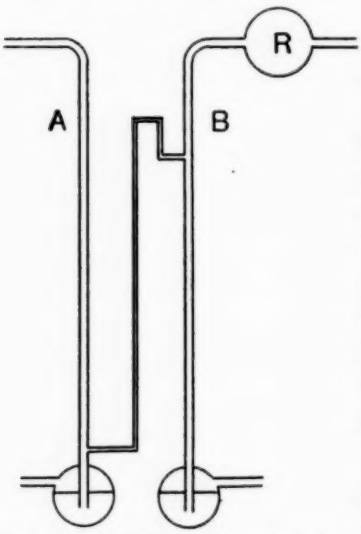


Fig. 2. Arrangement for admitting small quantities of gas.

Pyrex glass was used in the construction of the apparatus so that the copper parts could be baked out to 450°C. The vacuum was obtained by two mercury diffusion pumps in series, backed by an oil pump. To avoid gases from stop cock grease, mercury cut-offs were used in the high vacuum parts of the glass apparatus. These were separated from the part of the system containing the copper apparatus by a liquid air trap. A McLeod gauge, reading to 1×10^{-6} mm of Hg, was used to measure the pressure.

To admit small quantities of gas an apparatus shown in Fig. 2 was used. By adjusting the height of the mercury column A and lowering the column B, a known volume of 1 mm capillary tubing was filled with gas from the reservoir R. The pressure of the gas in R was usually about 1 or 2 cm of Hg. By raising the level of the mercury in B, this amount of gas could be forced into the space above A, which was connected to the high vacuum. In this way one could easily introduce just enough gas to make the pressure in the apparatus 1×10^{-3} mm of Hg, by changing the height of A and the pressure in R, the range of pressure produced by each operation could be varied indefinitely.

Method

If I_0 is the initial number of electrons in a beam sent through the gas and I the number still in the beam after it has passed through a distance x in the gas at a pressure p, then

$$I = I_0 e^{-\alpha x p}$$

where α is the absorption coefficient for the electrons at unit pressure of the gas. It is the total effective absorbing area in square centimeters of all the molecules in a cubic centimeter of gas at a pressure of 1 mm of Hg, when x is given in cm and p in mm of Hg. The effective absorbing area of a single molecule may be found by dividing α by 3.65×10^{15}, the number of molecules in a cubic centimeter of gas at a pressure of 1 mm of Hg.

By taking two sets of readings at different pressures two equations are obtained,

$$I_1=I_{01}e^{-\alpha x p_1} \quad \text{and} \quad I_2=I_{02}e^{-\alpha x p_1}$$

Solving these two equations for α gives,

$$\alpha=\frac{1}{x(p_1-p_2)}\log\left(\frac{I_1}{I_2}\cdot\frac{I_{02}}{I_{01}}\right).$$

In this equation only the ratio of the initial currents and of the final currents occur. The two readings of the micro-ammeter M, are proportional to the initial currents in the two cases and hence the ratio of the two readings may be used in place of the ratio I_{02}/I_{01}. The ratio of the two galvanometer readings is also equal to the ratio I_1/I_2.

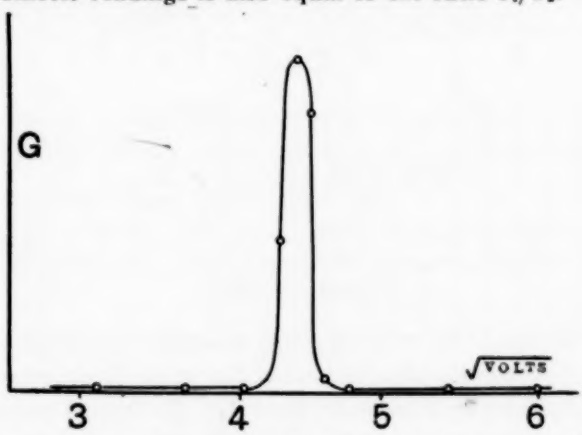


Fig. 3. Variation of the galvanometer deflection with square root of the accelerating potential, with constant magnetic field.

Because of the width of the slits, the voltage drop along the filament and the temperature distribution of velocities, galvanometer deflections were obtained for a range of values of the accelerating potential for a fixed value of the magnetic field as shown in Fig. 3. The reading M corresponding to the maximum deflection G of the galvanometer was recorded. A small quantity of gas was introduced, its pressure measured on the McLeod gauge and the corresponding readings of M and G recorded. If

the value of the log (M/G) is plotted against the product of the pressure and the distance, then α will be the slope of the line connecting any two observations taken at different pressures. Fig. 4 shows that α is practically independent of the pressure. The value of α was also found to be independent of the density of electrons in the beam. When M was increased from 1 to 5×10^{-4} amp., α remained constant.

Results

Argon, supposed to be 98 per cent pure, was taken from a bulb secured from the General Electric Co. The results of the measurements of α are shown in Fig. 5. The square root of the accelerating voltage is used as the abscissa because the velocity of an electron is proportional to the square

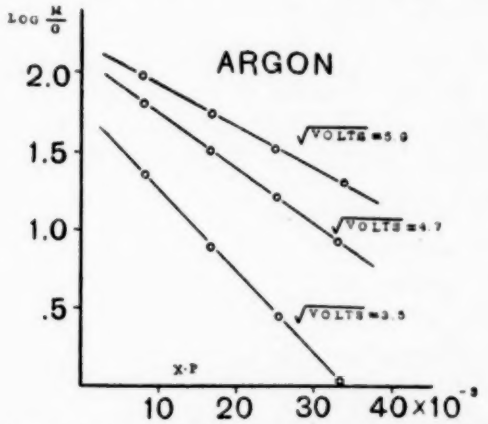


Fig. 4. Log of ratio of electron emission to maximum galvanometer deflection as a function of product of length of path and pressure, for three accelerating potentials in argon.

root of the voltage. The value of α was measured for velocities from 2 to 360 volts. The results obtained were found to check reasonably well with those obtained by Ramsauer, shown by the dotted curve.

Helium was obtained from the U. S. Government. It was further purified by passing it through a charcoal tube immersed in liquid air. The charcoal tube had previously been heated for several hours at 450°C. The results are shown in Fig. 5. Ramsauer's results are indicated by the dotted curve.

Methane, obtained from natural gas, was furnished by Dr. Glockler of the Gates Chemical Laboratory of this institute. It was further purified by liquifying with liquid air and then distilling. From Fig. 5 it can be seen that the curve is similar to that found for argon. The maximum absorption at 7.5 volts agrees very well with the value of 8 volts found

previously by Akesson. The pressure of the gas did not change when allowed to stand in the presence of the hot tungsten filament. If the gas were decomposed by the temperature of the filament an increase in the pressure should be observed.

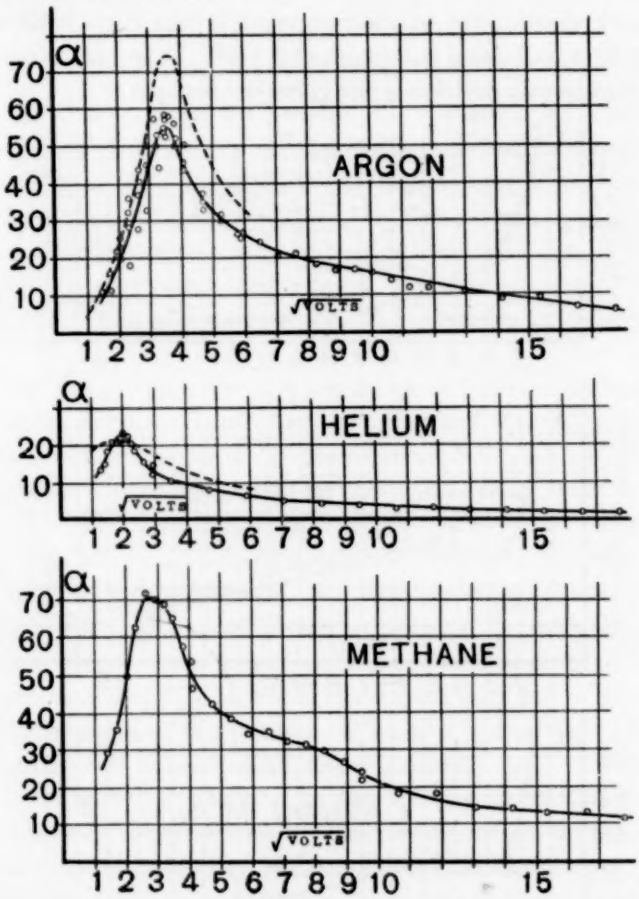


Fig. 5. Variation of absorption coefficient α in argon, helium and methane, with the velocity of electrons.

Hydrogen was dried and further purified by charcoal cooled with liquid air. Fig. 6 shows the values of α observed for hydrogen. The results are not in very good agreement with those of Ramsauer, shown by the dotted line. No maximum was observed in either case.

Nitrogen was prepared by the decomposition of ammonium nitrite. A water solution of this was heated and the resulting gas dried by passing it through a phosphorous pentoxide tube. The curve for nitrogen, Fig. 6, differs from any previous curve in that it has both a maximum and a mini-

mum. The minimum occurs at 9 volts which is near the resonance potential of the nitrogen atom, and the maximum at 18 volts which is near the ionization potential of the nitrogen atom. The determination of the maximum and minimum points was not sufficiently accurate to attach much significance to their occurrence near these critical points. Akesson's data indicate a maximum at 2 volts. A second maximum was also observed but its position is not given in his paper.

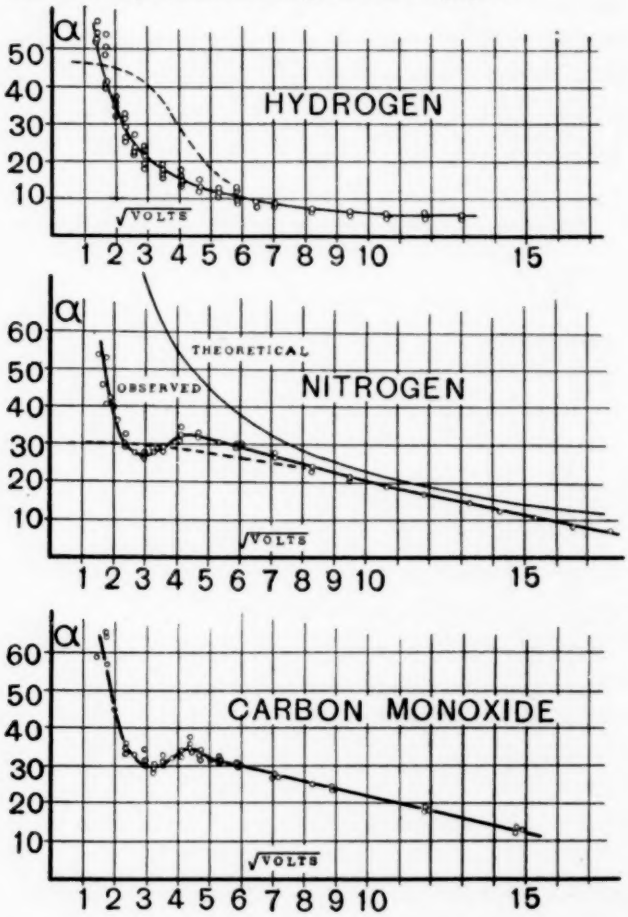


Fig. 6. Variation of α in hydrogen, nitrogen and carbon monoxide with velocity of electrons.

Carbon monoxide was prepared by the decomposition of formic acid on being dropped into hot sulphuric acid. The curve for carbon monoxide, Fig. 6, is seen to be almost identical with that obtained for nitrogen. The molecules of both gases consist of two atoms, each of which is supposed to have seven electrons. In the case of nitrogen the two positive

nuclei have each seven positive charges. In carbon monoxide one nucleus has six positive charges and the other eight. The similarity of the two curves indicates that the deflection of the slow speed electrons is determined chiefly by the field produced by the arrangement of the electrons in the molecule.

Theoretical Discussion

From the theory given by Zwicky[9] for the apparent absorption of electrons due to deflection in the field of a polarized molecule α should vary inversely as $\sqrt{V}$. Using the dielectric constant of nitrogen and the dimensions of the apparatus, $\alpha = 224/\sqrt{V}$. The relation between the computed and observed curves may be seen in Fig. 9. Using the dielectric constant of hydrogen and computing α, the above constant 224 is replaced by 150. This gives values of α that are about twice the observed values.

From this theory the value of α should never decrease with decreasing velocity of the electron. It can be shown that any attracting field that is independent of the orientation of the molecule will give a similar curve. For an inverse square attraction $\alpha = \text{const.}/V^2$; for an inverse cube law $\alpha = \text{const.}/V$; and for an inverse fifth power law $\alpha = \text{const.}/\sqrt{V}$.

Mayer[10] suggests as an explanation for the apparent maximum in nitrogen as observed by Akesson, that slow electrons in nitrogen have a selective reflection, i.e. do not attach so easily to the molecule to form a negative ion. But with the mean free path of the same order of magnitude as the total path length, one would not expect that half of the electrons would be reflected after two or more collisions into a collecting box whose opening subtended a small solid angle compared with the rest of the apparatus. A selective reflection for low velocity electrons requires that large numbers of negative ions should be formed at higher velocities. Because of their slower motion, the ions will remain in the beam for a comparatively long time and should have a large effect in increasing the effective absorption. Mayer found practically no change in α from 0.2 to 4 volts.

F. Hund[11] has proposed an explanation based on the quantum theory. He suggests that an electron whose kinetic energy is less than the amount of energy it would radiate if deflected, will not radiate but will continue undisturbed on its path. This explanation is suitable for the noble gases but will not explain the curves obtained for nitrogen and carbon monoxide.

[9] F. Zwicky, Phys. Zeit. **24**, 171 (1923).
[10] H. F. Mayer, Ann. der Phys. **64**, 474 (1921).
[11] F. Hund, Zeit. f. Phys. **13**, 241 (1923).

The number of ions formed, and consequently α, should increase as the density of electrons in the beam is increased. Measurements of α in nitrogen showed no such increase. The variation of α appears to be due to changes in the absorption coefficient and not to a selective reflection.

The author wishes to express his indebtedness to Dr. R. A. Millikan for suggesting this investigation and for his interest throughout the work.

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