INELASTIC COLLISIONS IN MERCURY VAPOR

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Abstract

A narrow beam of electrons from a hot cathode is taken from a space containing Hg vapor and is spread out into a spectrum in a magnetic field. The intensities of the components of the spectrum corresponding to energy losses equivalent to 4.9, 6.7 and 8.8 volts are measured as a function of the initial energy of the electrons. The intensity in each case reaches a distinct maximum within a few volts of the excitation potential of that component. Other energy losses are detected but have such low intensities that they are not measured.

Introduction

TWO closely related methods present themselves for the study of the mechanics of the valence electrons in the atom; the one the spectroscopic study of the light emitted, the other the electrical measurement of the energy losses of impacting electrons. The first, with its highly developed technique and high resolving power, has contributed most to our knowledge of the atom. The second, in spite of its vastly inferior ability to separate neighboring atomic states, has given us a direct verification of a fundamental hypothesis concerning the internal mechanics of the atom.

It should be pointed out, however, that the two methods do not measure quite the same thing. If we are interested in the mechanics of the collision between an electron and an atom it is to the electrical method, despite its poor resolving power, that we must go. The emission of radiation may be a very indirect consequence of the collisions, being subject to selection principles and to the effects of collisions of the second kind. The study of the residual energies of colliding electrons possesses the great advantage of directness in the study of collision problems.

White,[1] Valasek,[2] and Crozier,[3] have made spectroscopic studies of the intensity of the lines in the arc spectrum of mercury. By their experiments some light, rather indirect, has been thrown upon the relative frequencies of the various types of electronic collisions. Eldridge[4] devised a direct method of determining the probabilities of the collisions in mercury vapor. More recently Langmuir and Jones[5] have found values of the probabilities of the most prominent types of collisions in several gases, but only at voltages considerably higher than the ionizing potentials of the gases used. A more direct method than the one last cited and one that can be used at lower

[1] White, Phys. Rev. **28**, 1125 (1926).
[2] Valasek, Phys. Rev. **29**, 817 (1927).
[3] Crozier, Phys. Rev. **31**, 800 (1928).
[4] Eldridge, Phys. Rev. **20**, 456 (1922).
[5] Langmuir and Jones, Phys. Rev. **31**, 357 (1928).

voltage is desirable, and in this paper such a method and the results obtained by its use are described.

Apparatus

In the present experiment the electrons, after suffering collisions in mercury vapor, pass to a region of high vacuum and are there separated by a magnetic field into a "velocity spectrum." Hughes and Jones[6] have used a similar method with helium but without detection of any inelastic collisions.

The form taken by the apparatus can be seen from Fig. 1. The electrons emitted by the filament F are accelerated by a potential applied between F and the cylinder C. After numerous collisions with the mercury atoms a fraction of the current passes through the slit S. The magnetic field produced by the current in the coil M causes the electrons to move in circular paths as shown by the dashed lines. By proper adjustment of the magnetic field electrons of any desired energy may be caused to pass through the slit S' in

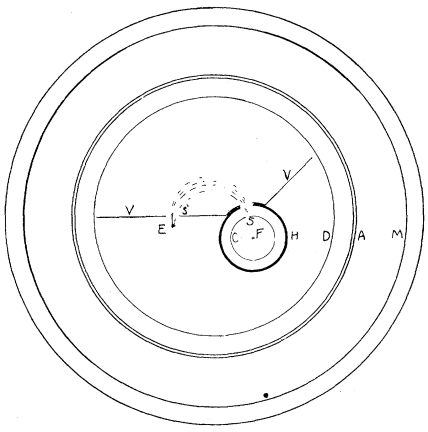

Fig. 1. Horizontal section of apparatus.

the vane V to the collector E, which is placed at the beam focus conjugate to the slit S. The current to E is measured by an electrometer shunted by a radio-active leak. A represents the wall of the evacuated tube and D is a metal cylinder which forms the wall of the deflection chamber.

The approximate dimensions and the materials used are as follows: F, 5 mm unthoriated tungsten wire 1 cm in length; C, molybdenum cylinder of 5 mm radius; H, copper tube of 8 mm radius; D, molybdenum cylinder of 6 cm radius; S, slit, 0.1×5 mm; S', 10×3 mm aperture in molybdenum vane; E, 20 mil molybdenum wire; distance S to S', 2 cm; coil M, 200 turns of 15 cm radius.

The radius of curvature, r, of the electronic orbit is given in terms of mass, velocity, charge and magnetic field by the expression $r=mv/eH$. Use of the energy equation $Ve=\frac{1}{2}mv^2$, gives

[6] Hughes and Jones, Phys. Rev. **29**, 214 (1927) (Abstract 31).

$$V = r^2H^2/2m.$$

Substituting the dimensions of the apparatus and reducing to practical units

$$V = 10.4I^2.$$

Here I is the current in the coil M, and V is the residual "energy in volts" of the electron as it emerges from the slit S.

This agrees with the observed relationship as shown in Fig. 2 except at low values of the field. The voltages are as read and neglect the initial velocity of the electrons at emission; as shown in Fig. 5, this amounts to about half a volt and will raise the observed (solid) curve to this extent but will still leave a puzzling difference between the curves. The observed curve may, however, be used to correlate energies with the deflecting fields.

In preliminary experiments it was found impracticable to locate a definite focus of the electron beam by purely geometric considerations; for this reason a flexible probe S is used which can be placed in any desired position

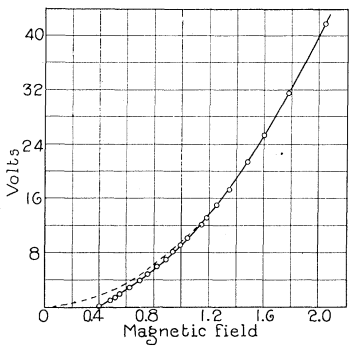

Fig. 2. Relationship between magnetic field and the energy equivalent in volts of the electrons collected.

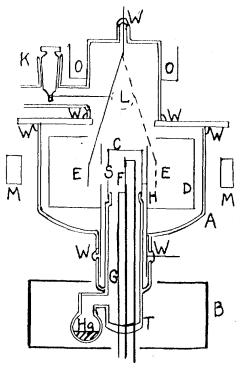

Fig. 3. Vertical section of apparatus. (Not drawn to scale.)

and by which the shape of the deviated beam can be explored throughout its path. This probe consists of a long wire operated by two threads wound on ground glass winches. The focus remains only approximately fixed as the voltage is changed, but it is not necessary to move the probe during a run.

The deflection chamber is large and of a single metal to avoid warping of the electron path by contact potentials.

Figure 3 is a schematic diagram to represent a vertical section of the apparatus. T is a glass tube, the top end of which is closed by the molybdenum cylinder C containing the slit S. On the axis of the cylinder and opposite the slit is a filament F. At the bottom of the tube T is a side tube containing mercury; by means of the electrical furnace B this can be heated to any desired temperature. T can be superheated by the 20 mil tungsten wire G. Inside the large glass tube A is the molybdenum cylinder D and the molybdenum vane V (shown in Fig.1.). D is partly closed at top and bottom and

serves to shield the region in which the electrons move. This shield is supported on a copper tube H which is waxed into the neck of the large glass tube. There is a window in H opposite the slit S. E is the collector, made of fine molybdenum wire fastened to piano wire. It can be moved to any desired position in the tube by means of the winches shown at K and L (L being similar to K). All of E except a 1.5 cm length at the tip is covered by a glass tube which in turn is covered by a grounded copper sheath. O is a container for liquid oxygen, W indicates sealing wax joints (water-cooled where necessary) and M is the coil furnishing the magnetic field.

It seemed *a priori* very probable that the electrons passing outward through the slit would be a fair sample of those present in the cylinder. As a matter of fact I found that, unless special precautions were taken, this was not the case and that an unduly small proportion of the slower electrons were received into the outer cylinder. As another illustration of this effect I may cite the following observation. With an ordinary three-element tube as used by Franck and Hertz it is customary to put a slight retarding potential upon the anode to discriminate against the lower electrons and so produce the characteristic peaks in the curve. While this is the theory

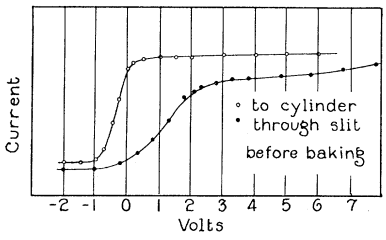

Fig. 4.

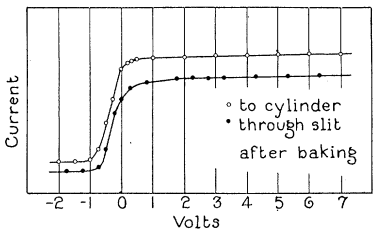

Fig. 5.

and the usual practice, it is often found that the tube works in very much the same fashion without the retarding potential; the slower electrons very largely fail to penetrate the grid. The reason for this is not altogether clear. With larger currents the space charge undoubtedly plays a role; also, surface contamination due in part to the thorium distillate from activated tungsten cathodes seems to have an important influence. As a result of preliminary experimentation, I found that the difficulty could be overcome by using small currents, using molybdenum for the metal parts, cleaning up the surface by cathodic bombardment and using unactivated tungsten for the cathode. (This was very kindly furnished by Dr. Saul Dushman of the General Electric Company).

Since the attainment of a neutral slit, that is, one which transmits slow and fast electrons in the same ratio as they are received by the cylinder as a whole, is the sine qua non of a quantitative method, and since this was obtained only after considerable experimentation, I show in Fig. 4 and Fig. 5 curves representing the behavior of the slit before and after bombardment. These curves were taken in the absence of mercury vapor. They show the current to the cylinder C, and to a different scale, that through the slit

to the cylinder D from an unactivated tungsten filament. Both curves in Figure 5 show satisfactory saturation characteristics after the cleaning process; before baking out (Fig. 4) the slower electrons cannot penetrate the slit. Curves taken with activated filaments or with larger currents show extremely bad characteristics.

The region inside the cylinder C should be as nearly equipotential as possible. Under the conditions of the experiment the effect of space is negligible and the potential is that of the cylindrical condenser. With the present dimensions this gives a potential within 20 percent of that of the cylinder 2 mm from the cathode which is not unsatisfactory.

Electrons upon striking the probe or other part of the tube may be either reflected without velocity loss (as in the Davisson-Germer experiment) or cause the emission of very slow electrons. This last effect is very important and may give a reversal in the current to the collector when the incident energy is above 20 equivalent volts. The effect could probably be avoided by using a small Faraday cylinder for collector; the difficulty can also be overcome by giving the collector a small positive potential. The latter was the method used in this experiment.

Experimental Results

The curves obtained in one of the runs are shown in Fig. 6. The mercury was at a pressure corresponding to a temperature of 94°C, at which pressure the mean free path, while depending somewhat on voltage, is low enough so that the average electron escaping from the cylinder has made several collisions and the number does not vary markedly with voltage.

Ordinates on the curves are proportional to the current to the conductor. The upper row of abscissas gives the current in the field coil; the lower row gives the energy equivalent in volts of the electrons collected. The accelerating potential is indicated at the right of each curve. The peaks due to those electrons which have made only elastic collisions are not completely drawn in but the maximum height of each is indicated in units equal to those in which the sheet is ruled.

The principal peak, corresponding to electrons which have suffered no energy losses, appears at increasingly higher magnetic fields as the accelerating potential is raised, in accordance with the relationship between field and voltage given in Fig. 2. The marked increase in height of this peak will be discussed later.

The curve for 5 volt electrons shows that, within the limits of measurement, all of the collisions are elastic. (It is important here to remember that the chamber is not strictly equipotential). The curve for 5.5 volts shows, in addition to the main peak, a small but distinct peak appearing at that value of the field which brings to the collector electrons of about 0.5 volts energy. This peak is due to those electrons which have lost 4.9 volts at collisions with mercury atoms inside the cylinder. At 6 volts this peak has increased in size and, since it now represents 1.1 volt electrons, appears at a slightly higher field. It continues to increase in size for a few volts but beginning with the 10 volt curve it becomes of less importance.

The curves for 7 and 8 volts show a partially resolved peak on the left side of the peak due to the 4.9 volt losses. It corresponds to an energy loss of about 5.7 volts but is more probably due to the excitation of the metastable 2^3P_3 level which requires a loss of 5.45 volts. It is so poorly resolved that no attempt is made to measure its importance in a quantitative manner.

The curve for 8 volts shows a small third peak corresponding to electrons which have between 1 and 2 volts of energy and which is to be identified

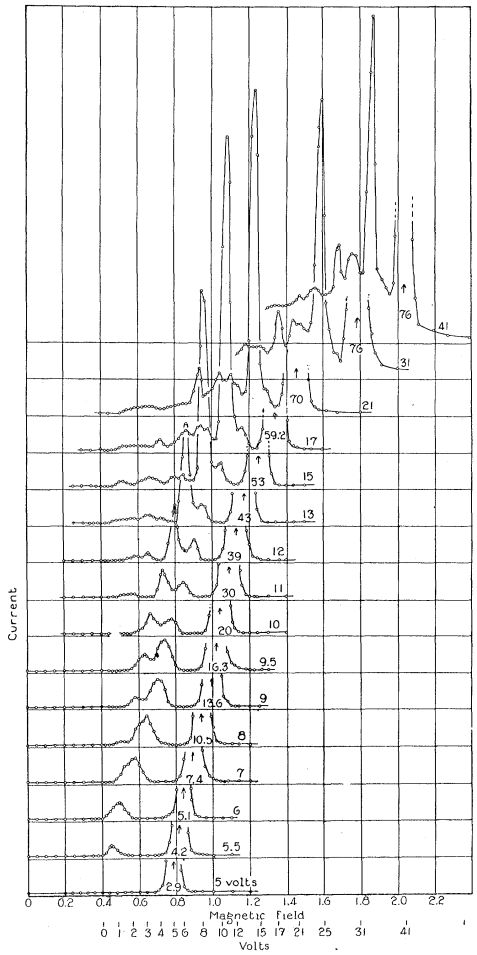

Fig. 6. Set of curves taken with Hg present at a temperature of 94°C.

with the 6.7 volt loss. This type of collision is seen to be improbable at voltages slightly above the critical value but the peak increases in size more or less steadily up to as high values as were used in this experiment. At 15 volts and above, it is by far the most important of those peaks due to inelastic collisions.

The curves in Fig. 8 show no evidence of losses of 7.7–7.9 volts, corresponding to transitions to the 2^3S or 2^1S states. This type of collisions must

be rather unlikely, the neighboring 6.7 volt peak hiding whatever trace of it there may be present. A peak showing losses of approximately 8.8 volts appears above 11 volts (see the 3 volt peak on the 12 volt curve).

Above this occur two peaks which are not positively identified; in the 15 volt curve peaks appear at 5.3 and 3.4 volts, corresponding to losses of 9.7 and 11.7 volts. The former may be due to double 4.9 volt losses and the latter to a 6.7 and a 4.9 volt combination. The first of these persists at higher voltages and appears at approximately the proper position. It is difficult, however, to identify it with the multiple 4.9 volt losses at these higher voltages since with increasing voltage such losses become increasingly improbable; in the 21 volt curve this peak is more prominent than the peak due to single 4.9 volt losses. The second peak, which at 15 volts is probably due to 6.7 and 4.9 volt combination, changes its relative position at higher voltages and appears then to represent a loss of about 10.8 volts. A peak is found with great consistency in this position in curves taken at other temperatures. At 31 volts this peak is comparable in height with the

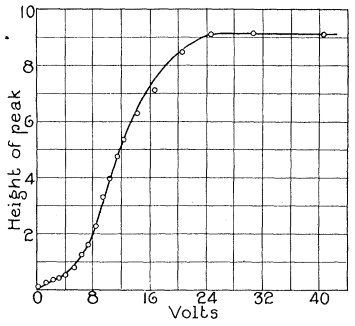

Fig. 7. The calibration by which the heights of the peaks in Fig. 6 are corrected before plotting the curves in Fig. 8.

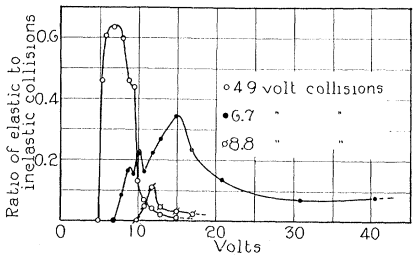

Fig. 8. The most probable type of collisions and the variation of the likelihood of each as the energy of the colliding electrons is varied.

one representing two 6.7 volt losses. It seems unlikely that at these higher voltages the peak is due to the 6.7 and 4.9 volt combination; it may be due to 10.4 volt losses involving ionization.

The other peaks in the higher voltage curves are due to electrons which have made more than one inelastic collision involving the loss of 6.7 volts.

In analyzing the curves of Fig. 6 account is first taken of the fact that the apparatus does not collect slow and fast electrons with the same effectiveness. In order to correct the curves in Fig. 6 for this effect the heights of the current peaks for voltages from 0 to 40 are recorded under conditions identical with those obtaining when the data for Fig. 6 were taken. From Fig. 7 the heights of the peaks in Fig. 6 are corrected. The areas under the corrected peaks are measured and the ratio of the area due to those electrons which have lost 4.9 volts to the area due to those which have lost no energy at all is calculated for each value of accelerating potential used. This ratio is shown as a function of accelerating potential in Fig. 8, with similar curves for the 6.7 and 8.8 volt types of inelastic collisions.

The three curves in Fig. 8, while resembling each other in that each shows a distinct maximum, differ in at least one important respect. This is their behavior near their critical voltages. The one representing the 4.9 volt energy losses has attained its maximum value within less than three volts of its critical voltage, while the curve for the 6.7 volt losses and the 8.8 volt losses is less striking but is still quite distinct.

The reasons for the irregularities in the curves between 8 and 11 volts are not understood, but since they consistently appear in other sets of curves taken under varying conditions, I believe they have some real significance.

Discussion

A very fundamental discrepancy seems to exist between these results and the photoelectric curves shown by Franck and Einsporn.[7] From the experiments of these investigators one is led to believe that a great variety of types of collision exist with substantially equal probabilities; that in every case the excitation function rises with great suddenness as the critical energy is exceeded and within a fraction of a volt appears in many cases to drop off again. This is quite a different picture from that which one obtains from the present observations. Here we find three types of collision of preponderating importance. In the case of the 6.7 volt and 8.8 volt types the collisions appear relatively improbable at voltages slightly above the critical value and it is not easy to see how the sharp breaks in the photoelectric curves can be accounted for.

It is very difficult to reconcile the two experiments. The one seems to show without question that most of the collisions involve either 4.9 or 6.7 volt losses, the other that photoelectric emission occurs or metastable atoms are created at a great number of critical potentials. An unlikely hypothesis is that the energy losses occurring at these voltages are in every case of the 4.9 or 6.7 volt type. A somewhat more probable explanation would be that the many other collision types of Franck and Einsporn occur only in the very close neighborhood of the critical voltages and disappear as that voltage is slightly exceeded. Such collisions would then be indicated by electrons of nearly zero velocity in my experiment and might not have been detected, since my apparatus collects such electrons rather inefficiently. There is no collateral evidence to support this view, and it may seem a very unlikely one. But, however unlikely, no other hypothesis seems to give a more reasonable hope of correlating the photoelectric work of Franck and Einsporn (which has been verified by others) on the one hand, and on the other, the many experiments on inelastic collisions.

In conclusion, the writer wishes to acknowledge his indebtedness to the members of the staff of the Department of Physics at the State University of Iowa for their patient, cheerful and invaluable assistance. To Professor J. A. Eldridge, who suggested the problem and supervised the work, his debt is particularly great.

[7] Franck and Einsporn, Zeits. f. Physik **2**, 18 (1920).