The ratios W_{gas}/W_{air} are in excellent agreement with the ratios determined by Jesse and by Failla; in both their determinations the stopping power ratio did not enter into the calculations since the total electron energy was absorbed in the gas. In our determination, however, it was necessary to use the stopping power ratios since only a fraction of the electron energy was expended in the gas. The excellent agreement between the two methods indicates that the error in the calculation of the stopping power ratio is small. The absolute values of W for the different gases are also in excellent agreement with Jesse's results; the value of 25.5 ± 0.3 ev obtained for argon is probably low because of the extreme sensitivity of argon to impurities. It should be pointed out that both Jesse and Failla used low-energy electrons in their investigations; these results include considerably higher electron energies. The accuracy of the absolute values of W is, of course, dependent upon the accuracy of the value of G and the calculated stopping power ratios which are used, and also upon the purity of the gases. Further experiments are planned in which the stopping power ratios will be experimentally determined and the purity of the gases will be carefully controlled.

ACKNOWLEDGMENTS

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Measurement of Absorption Coefficients for Photoionizing Radiations in Low-Pressure Gases with a Space Charge Detector*

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A Kingdon cage space-charge detector has been used to measure the production of positive ions in a low-pressure gas due to absorption of photons produced by electron impact excitation in another region of the same gas. Absorption coefficients were measured by changing the source to detector separation. High-purity vacuum techniques were used to avoid contamination of the gas. No ionization was found in hydrogen. For nitrogen the molecular cross section was 4.1×10^{-16} cm^2 and for argon the atomic cross section was 3.1×10^{-16} cm^2. Tentative suggestions are made as to the processes responsible for these total absorption cross sections being much larger than the photoionization cross sections for monochromatic radiations in the ionization continuum region.

THE role of photoionization as an important secondary mechanism in gas discharges, particularly near the anode in asymmetric fields as in the burst pulses and streamers of positive point corona has been extensively discussed by Loeb.[1] A large number of measurements have been made of the absorption coefficients for the radiations producing such photoionization under discharge conditions.[2] Such measurements when carried out at high pressures do not allow accurate evaluation of the very high absorption cross sections required to explain the small distance scale of the burst pulses and streamers. In making measurements at lower pressures it is important to see that any currents measured are due to photoionization arising in the gas and not from photoelectrons emitted from electrodes or walls. The space-charge detector of Kingdon[3] and Hertz[4] seemed ideally suited for this purpose. This operates on the principle that introduction of a few positive ions into the electron space charge of a space charge limited diode gives a large increase in the electron current. The amplification so obtained makes it possible to detect positive ions in the presence of slow electrons.

The Kingdon cage was first applied to the detection of photoionization in gases and vapors by Mohler.[5] It was adapted for measuring relative cross sections for photoionization in alkali vapors by Lawrence and Edlefsen[6] who used two diodes with a balanced technique to eliminate fluctuations due to variations in

* This work was supported by the Office of Naval Research.
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[1] L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, Inc., New York, 1939), Chap. X, Sec. 8, pp. 520 ff.; L. B. Loeb, Phys. Rev. **73**, 798 (1948); **94**, 224 (1954).

[2] E. Greiner, Z. Physik **81**, 543 (1933); A. M. Cravath, Phys. Rev. **47**, 254 (1935); G. Dechene, J. phys. radium **7**, 533 (1936); H. Raether, Z. Physik **110**, 611 (1938); W. Schwiecker, Naturwiss. **28**, 380 (1940); Z. Physik **116**, 562 (1940); S. H. Liebson, Phys. Rev. **74**, 694 (1948); Jaffe, Craggs, and Balakrishnan, Proc. Phys. Soc. (London) **B62**, 39 (1949).

[3] K. H. Kingdon, Phys. Rev. **21**, 408 (1923).

[4] G. Hertz, Z. Physik **18**, 307 (1923).

[5] F. L. Mohler, Phys. Rev. **28**, 46 (1926); Proc. Natl. Acad. Sci. U. S. **12**, 494 (1926).

[6] E. O. Lawrence and N. E. Edlefsen, Phys. Rev. **34**, 233 (1929).

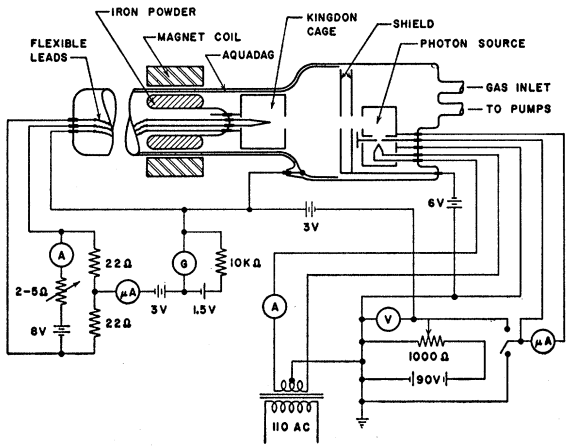

FIG. 1. Cross section of experimental tube with circuit diagram.

filament current or vacuum conditions. In this form it was used in gases by Varney and Loeb.[7] Berry and Varney[8] later showed that traces of oxygen caused much of the fluctuation and that under the purest conditions the use of a second balance diode was not needed.

APPARATUS

A cross section of the experimental tube is shown in Fig. 1 which includes a circuit diagram showing the electrical connections to the various elements. All electrodes except for tungsten filaments were made of nickel sheet. The Kingdon cage was mounted on a glass slider in which iron powder was sealed to enable the position of the detector to be adjusted by an external magnet. Electrical connections to the detector were made by flexible copper leads insulated by glass beads. Unfortunately these provided a variable leakage resistance between the anode and cathode leads which caused considerable noise in the detector circuit along with zero shift whenever the detector was moved. The noise prevented using the galvanometer at high sensitivity so most measurements were taken with a sensitivity of 0.2 μa/cm.

The photon source produced radiation by excitation of the gas contained in a field-free box through bombardment by an electron beam of variable energy. Photons from the source reached the detector through collinear holes in the source, isolating shield, and detector. The tube was made of borosilicate glass. The inside of the wall in the region between the isolating shield and the detector was coated with aquadag to prevent the formation of wall charges which might cause spurious currents in the detector. There was a narrow longitudinal stripe cleared through the aquadag so that the separation between source and detector could be found by measuring the distance between two fiducial marks, one on the glass slider on which the detector was mounted and the other on the tube wall.

Potentials on the various elements of the tube were arranged so that neither electrons nor positive ions from the source could reach the detector and that positive ions formed in the gas between the shield and detector would be driven away from the detector. When the voltage on the source was removed to check the detector zero, the Kingdon cage circuit was left at the same voltage with respect to ground to prevent leakage currents from changing.

The experimental tube formed part of a high-purity vacuum system arranged for taking measurements of photoionization under dynamic conditions of gas flow through the tube. The gas was admitted to the tube from glass flasks through a vacuum valve of the Alpert[9] type. The pressure in the experimental tube was adjusted by use of a second vacuum valve between the tube and a liquid nitrogen cooled trap preceding a mercury diffusion pump. Before admitting each gas the experimental tube was outgassed by baking at 400°C along with the valves, a Westinghouse WL-5966[10] ionization gauge and an RCA 1936 thermocouple gauge. After bakeout the metal elements of the tube were further outgassed by the use of a small induction heater. The outgassing procedure was continued until with all filaments in the tube hotter than for normal operation the background pressure was less than 10^{-8} mm. The gas supply flasks were equipped with break-offs which were opened after the outgassing was completed by the use of glass encased iron slugs moved by an external magnet. For each gas used the thermocouple gauge was calibrated against a McLeod gauge which was connected to the vacuum system on the pump side of the cold trap. This calibration was done essentially under static conditions and the results were then used to read the pressure under the dynamic flow conditions. The vacuum system was continuously pumped from the start of the outgassing procedure until measurements on the gas were completed.

Absorption measurements were taken by adjusting gas pressure, source voltage and current to the desired values, setting the Kingdon cage filament current so that the current through the galvanometer connected in the bucking circuit was small. The galvanometer then measured essentially all the change in plate current of the detector diode. For a number of separations between source and detector the galvanometer reading was taken with source voltage on and off. The difference between these readings was taken as proportional to the ionization produced in the detector as had been found by Lawrence and Edlefsen.[6]

Since the solid angle which the entrance hole for photons in the detector subtends at the source is a function of distance, the relationship between the galvanometer deflection Δ and the separation x between

[7] R. N. Varney and L. B. Loeb, Phys. Rev. **48**, 822 (1935).
[8] H. W. Berry and R. N. Varney, Phys. Rev. **57**, 1063(A) (1940).
[9] D. Alpert, J. Appl. Phys. **24**, 860 (1953).
[10] R. T. Bayard and D. Alpert, Rev. Sci. Instr. **21**, 571 (1950).

source and detector will be of the form

$$x^2\Delta \sim e^{-\mu x},$$

where μ is the effective total absorption coefficient in cm^{-1} for the radiation responsible for the photoionization. Thus a semilogarithmic plot of $x^2\Delta$ against x gives a value of μ from the slope of a straight line fitting these points. To compare the amounts of photoionization under different conditions, for each run the value of $x^2\Delta$ at $x=3$ cm taken from the straight line was recorded as I, the intensity of photoionization. Figure 2 shows examples of these logarithmic plots for two pressures of nitrogen. These are reasonably linear although the range of separations is hardly adequate for a definitive test. This occurred because the arrangement of the flexible leads to the detector did not allow greater motion.

RESULTS AND DISCUSSION

Nitrogen

Unlike the result of Varney and Loeb[7] who found only very weak ionization in nitrogen, a considerable ionization has been found in this study. Professor Loeb states that it is probable that their studies were carried out nearer threshold energy and at somewhat higher values of pressure times distance which would have militated against their having observed this phenomenon.

Figure 3 shows the absorption coefficients obtained as a function of pressure for Airco "reagent grade" nitrogen for a series of runs at a source voltage of 50 volts and a source electron current of 200 μa. Results appeared to be very similar at other voltages and currents and also for tank nitrogen which had been passed over hot copper and through a cold trap into a previously baked out flask which was sealed off when filled and later opened in the same manner as the commercial flask. No measurements of absorption coefficients could be obtained for source voltages near threshold because of the small signal to noise ratio.

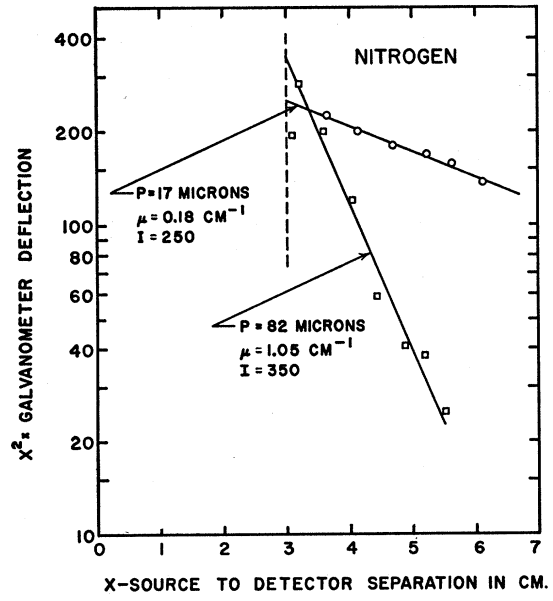

FIG. 2. Semilogarithmic plot showing evaluation of absorption coefficient and intensity of photoionization.

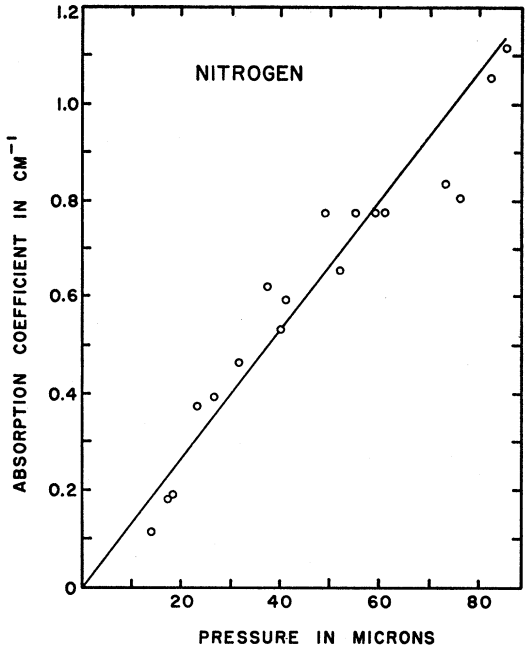

FIG. 3. Absorption coefficient as a function of pressure—nitrogen.

The absorption coefficients give a molecular cross section of 4.1×10^{-16} cm^2 independent of pressure as compared with the value of 2.5×10^{-17} cm^2 found by Weissler and his co-workers[11] for the photoionization continuum. They did find a total cross section of 1.0×10^{-16} cm^2 at a point about 0.5 A from the head of an unclassified absorption band found by Worley[12] at 765 A. There may also be other features in this wavelength region with even higher absorption cross sections. Thus it may be possible that the ionization measured here is due to photoionization directly by absorption of photons emitted from states of neutral nitrogen of greater energy than the lowest ionization potential. The ionization cross section in this region is only a part of the total absorption and the light output of the source at this wavelength seems likely to be small, although a knowledge of the distribution of light from a source like that used here would be of interest. *Note added in proof.*—In a private communication, Weissler states that Maunsell's data include Worley's band[12] which Weissler's data did not and that Maunsell's value may well be correct.

The experimental intensity of photoionization is shown as a function of pressure by the points in Fig. 5.

[11] Weissler, Lee, and Mohr, J. Opt. Soc. Am. **42**, 84 (1952); Wainfan, Walker, and Weissler, J. Appl. Phys. **24**, 1318 (1953).
[12] R. E. Worley, Phys. Rev. **64**, 207 (1943).

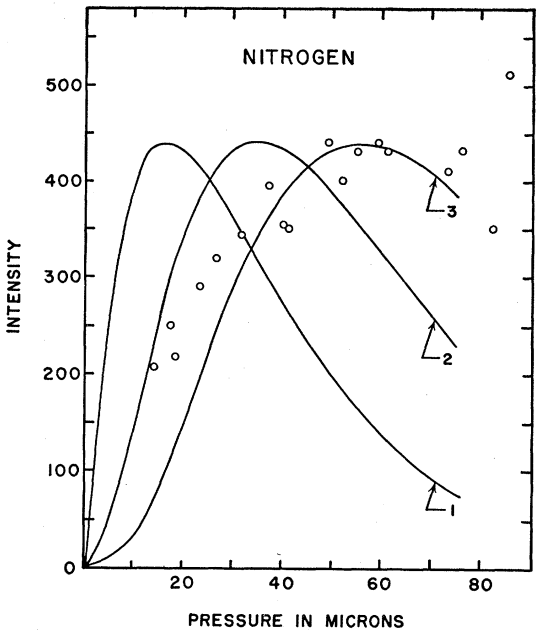

FIG. 4. Intensity of photoionization as a function of pressure—nitrogen. The points are experimental, the curves are theoretical for different degrees of pressure dependence.

These appear to show a flat maximum near $p=55$ microns with $I=440$. An attempt was made to see if some idea of the process of photoionization could be discovered by a study of this. With a photon source independent of gas pressure and a direct photoionization process, the number of positive ions produced in a detector of length l at a distance x from the source will be given by a relation of the form

$$I\sim e^{-\mu x}(1-e^{-\mu l}). \tag{1}$$

With a source of the type used here the light output would be expected to be proportional to pressure, p, so that one should have

$$I\sim pe^{-\mu x}(1-e^{-\mu l}). \tag{2}$$

If the ionization process requires a collision between an excited and a normal molecule then an extra factor proportional to pressure is required to give

$$I\sim p^2e^{-\mu x}(1-e^{-\mu l}). \tag{3}$$

With the use of the linear relation between μ and p of Fig. 3 and adjusting to the amplitude of the observed maximum the curves of Fig. 4 were calculated. The position of the maximum fits the higher-pressure dependence of curve 3 but the lower-pressure points lie above it. Probably the assumptions on which the calculations were based are oversimplified but the results do indicate that there may well be pressure dependent effects involved. Of course, since both source and detector are operated at the same pressure, it is impossible to state in which the pressure dependence is occurring.

When measurements on one flask of pure nitrogen were completed about 0.1 percent hydrogen was added by breaking open a small tube of hydrogen by an iron slug. 0.5 percent oxygen was added to another flask by the same technique. These experiments were tried to see if there was any change in the ionization of the resulting mixed gas by the well-known ionization of impurities by collision with excited states of the main gas. No such effect was noted probably because of the rapid clean up of both hydrogen and oxygen by the tungsten filaments as discussed by Dushman.[13] Also even if the hydrogen were not completely cleaned up, the fact that its ionization potential is very close to that of nitrogen would not be expected to lead to much extra ionization since there are not enough highly excited nitrogen states to ionize hydrogen.

Hydrogen

Tank hydrogen which had been purified by passing over hot copper and through a cold trap before being sealed into a previously baked and evacuated flask was used. Considerable cleanup occurred on turning on the filaments but by increasing the flow rate any desired pressure could be maintained. No photoionization could be observed at any pressure up to 60 microns, in agreement with the result of Mohler.[5] Adding 0.1 percent nitrogen did not produce any ionization which is not surprising, since the ionization potential of nitrogen is higher than that of hydrogen and thus photons which cannot ionize hydrogen should not be expected to be able to ionize nitrogen.

Argon

In conformity with the results of Mohler[5] and of Varney and Loeb,[7] ionization was observed in argon. For Airco "electronic grade" argon the absorption coefficient as a function of pressure is shown in Fig. 5. For pressures below 30 microns, an atomic cross section of 3.1×10^{-16} cm^2 seems satisfactory but the effective cross section at higher pressures is less than this. A theoretical photoionization cross section of 3×10^{-17} cm^2 at the ionization limit has been estimated by Dalgarno.[14] Wainfan, Walker, and Weissler[15] found 1.7×10^{-17} cm^2 near the threshold and values in the range 1.0–2.5×10^{-17} cm^2 at wavelengths to 473 A. The total absorption cross section will be higher than this photoionization cross section at lines in the region between the two series limits, but a direct photoionization process would not be expected to give much production of positive ions.

There are at least two complex processes by which absorption of photons of the resonance series with energies less than the atomic ionization limit can pro-

[13] Saul Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, New York, 1949), Chap. X, Sec. 5, pp. 673 ff.

[14] A. Dalgarno, Proc. Phys. Soc. (London) **A65**, 663 (1952).

[15] Wainfan, Walker, and Weissler, Gaseous Electronics Conference, 1954, Paper F2 (unpublished).

duce ionization. One of these is the pressure dependent mechanism of Hornbeck and Molnar,[16] by which an argon atom excited to within about 0.7 volt or less of the ionization limit can produce an ionized molecule by collision with an unexcited atom. This could lead to photoionization by the process

$$A+h\nu\rightarrow A^*,$$
$$A^*+A\rightarrow A_2^+ +e.$$

Another possible process which could involve the same states would involve ionization of a photoexcited atom by impact with one of the relatively low energy electrons of the detector. This reaction would be

$$A+h\nu\rightarrow A^*,$$
$$A^*+(e+\text{K.E.})\rightarrow A^+ +2e.$$

This process could act, not as a secondary mechanism, but only to increase the first Townsend coefficient. Mechanisms like these could explain the observed decrease in cross section at higher pressure by an increased contribution either from the wings of the lines involved or from more weakly absorbed lines.

A decision as to the type of ionization produced might be made by an accurate pressure-dependence study at low pressures where the noise level of the present apparatus did not allow accurate measurements to be made. A fitting to theoretical intensity curves of the type tried for nitrogen cannot be used for argon because the absorption coefficient is not linear with pressure. Another possible way of getting at the process responsible might be a mass spectrometric analysis of the ions produced.

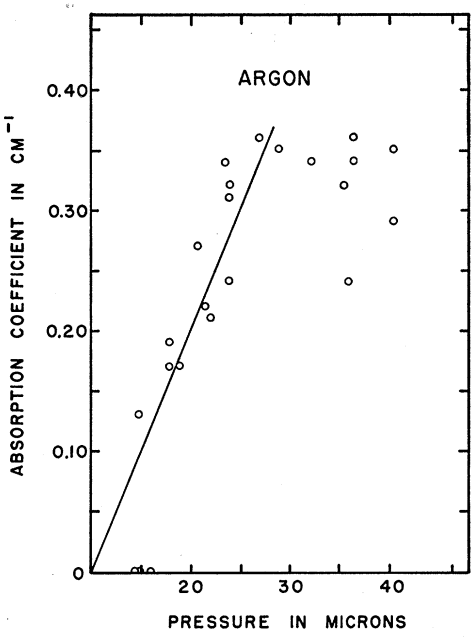

FIG. 5. Absorption coefficient as a function of pressure—argon.

[16] J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 621 (1951).

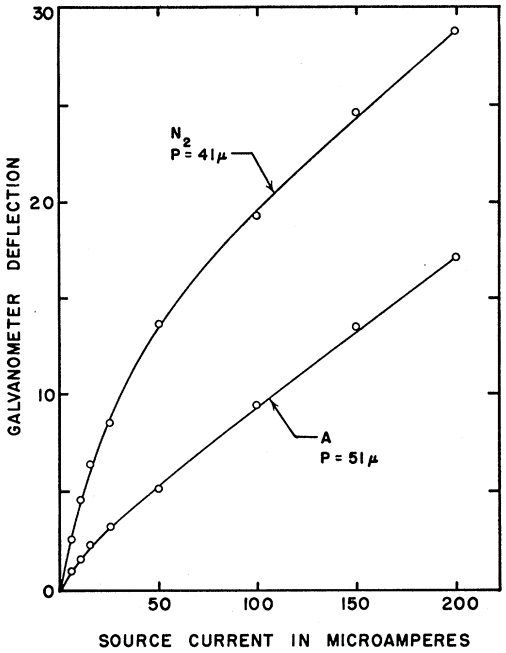

FIG. 6. Photoionization as a function of source current.

0.1 percent nitrogen added to the argon produced no noticeable changes, so that excited states of argon could not produce much ionization of nitrogen, probably because of the small difference in ionization potential.

Variation with Source Conditions

Figure 6 shows the variation of the galvanometer deflection as the current was changed in the exciting electron beam. For these curves the source voltage was fixed and the detector was not moved between readings. For neither nitrogen nor argon is the dependence linear as might be expected for a single-photon process nor steeper than linear as would be caused by a multiple-photon process. For both the curvature is like that for some sort of saturation process and is much more pronounced in nitrogen than in argon. It cannot be definitely stated whether the cause of this arises in the source or detector. If it is due to a nonlinearity in the detector, this would require a correction to be made to the points from which the absorption coefficients were calculated. This would have the effect of increasing the coefficients above those shown earlier so the cross sections shown should be considered as minimum values. At the same time, correcting the points would make the curves less linear, becoming steeper at greater separations. This is the opposite effect to that to be expected from a superposition of absorptions of different radiations where the effective absorption coefficient becomes less at greater distances. The assumption that the nonlinearity is in the source leads to less difficulty. Here it is possible that space-charge effects can cause a spreading of the electron beam and hence of the

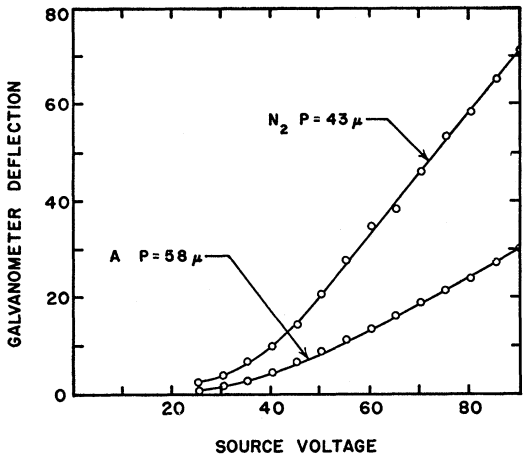

FIG. 7. Photoionization as a function of source voltage.

region of gas-emitting radiation. Since the photons are collimated at the source such spreading would cause a decrease in the efficiency of the source with increasing current. The lower curvature in argon could be due to the greater effective cross section in argon than in nitrogen for ionization by 50-volt electrons.[17] The greater number of positive ions formed would produce less spreading of the electron beam. Unfortunately the geometry of the source is not conducive to calculating the distribution of excitation in the source.

The variation of photoionization with the voltage accelerating the source electron beam is given in Fig. 7. The source current of 100 μa used for these curves could not be maintained at low source voltages, but tests in this region with lower currents indicated that the detector response approached zero slowly as the voltage neared the ionization potential with no sharp threshold. Some of the tests were made with a pulsed-filament supply so that the electron beam did not have a spread in energy due to the voltage drop along the source filament. The excitation curves do not resemble those for excitation or ionization of a single state, which show a well-defined threshold followed by a rapid rise to a maximum. Instead they look more like the total excitation cross-section curves of Maier-Leibnitz,[18] which however extended for only a few volts above the ionization energy.

CONCLUSIONS

The fact that the absorption coefficients measured in this study for radiations producing photoionization in gases are considerably larger than those determined for monochromatic radiations of energy greater than the ionization potential indicates that under gas discharge conditions the process of photoionization may be a complex one. Ionization produced through photoexcitation followed by molecular ion formation by a process like that of Hornbeck and Molnar[16] might produce secondary electrons in uniform fields and does act as a secondary mechanism leading to self-sustaining discharges in asymmetric fields. At the same time the other complex ionization process discussed earlier in which low-energy electrons ionize the photoexcited states can only act to augment the primary ionization process where there is already a supply of electrons. In any event, processes such as the Hornbeck and Molnar and the Penning effects increase the first Townsend coefficient as statically measured from two to twenty fold. It is not difficult to account for the large observed cross sections with the aid of such indirect processes in addition to the direct process.

The mere observation of ionization due to photon absorption in a study of this type does not prove that it will be important as a secondary process in gas discharges, since the low-energy electrons of the Kingdon cage may be involved. On the other hand, if ionization is not observed there is no guarantee that it may not be important in discharges at higher pressure. This can occur since materially lower absorption cross sections would reduce the amount of ionization below that observable here. In addition there might be other pressure-dependent effects involved.

One especially interesting field in which photoionization has been invoked as a mechanism is the positive point corona with burst pulses and streamers in oxygen, air, and other mixtures containing oxygen. This has been extensively discussed by Loeb.[1] It would thus be of great interest to study the photoionization in oxygen and other gases containing oxygen. This cannot be done by the Kingdon cage technique as used here because of the reaction of the oxygen with the tungsten filaments.

ACKNOWLEDGMENTS

I deeply wish to thank Professor Leonard B. Loeb who suggested and directed the work on this problem for his continued advice and encouragement during the course of this research. I also wish to thank the present and former members of his research group for many helpful discussions, especially Dr. J. H. Parker for advice on vacuum technique and gas-handling procedure. I am grateful to the Physics Department glassblower Mr. M. R. Corbett for much skillful work.

[17] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, 436 (1925); **27**, 724 (1926).
[18] H. Maier-Leibnitz, Z. Physik **95**, 499 (1935).