PHOTO-ELECTRIC IONIZATION OF CAESIUM VAPOR*

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Abstract

Measurement of photo-electric ionization in gases.—The current from a filament, normally limited by space change, is increased by the presence of positive ions. As shown by Kingdon this effect may be greatly magnified if a small cathode is practically enclosed by the anode so that the ions are imprisoned. This method was used for the detection of photo-electric ionization. Besides possessing extreme sensitivity it is unaffected by photo-electric emission from the electrodes.

Photo-electric effect in caesium vapor.—The change in thermionic current with the unresolved radiation from a mercury arc was measured as functions of the applied voltage, filament temperature, and vapor pressure. Then the photo-electric effect as a function of wave-length was studied using a monochromatic illuminator to disperse light from the arc or a Mazda lamp. The ionization per unit flux was found to increase with increasing wave-length to a sharp maximum at the limit $1s = 3184$A of the principal series, as is required by the Bohr theory. For longer wave-lengths the ionization decreased to about 10 percent at 3400A. *Photo-excitation.* The simple theory does not admit of ionization by wave-lengths greater than 3184A but the data are in qualitative agreement with the hypothesis that such radiation produces excited atoms which upon collision with other atoms acquire sufficient additional energy to become ionized. Hence, unlike an x-ray limit, the photo-ionization effect for a valence electron is not sharply discontinuous at the true threshold for direct ionization.

Photo-ionization photometer and intensitometer. A tube of the type described, with suitable gases for the range of wave-length involved, may be used as a photometer or may be calibrated to measure intensity of radiation directly.

Historical Summary

THE status of the subject of the photo-electric effect in vapors, up to 1922, was summarized in Chapter X of the Origin of Spectra.[1] Here it was pointed out that while all direct experiments had failed to demonstrate the existence of the phenomenon, its presence was indicated by the continuous absorption, exhibited by a monatomic vapor, of frequencies greater than that corresponding to the highest term in the arc spectrum.

Since then much more satisfactory evidence for the continuous absorption has been obtained by Harrison[2] who has made quantitative measure-

* Published by permission of the Director of the Bureau of Standards, Department of Commerce.

[1] Foote and Mohler, Origin of Spectra Chemical Catalog Co., New York.

[2] Harrison, Phys. Rev. **24**, 466 (1924).

ments of the transmission of sodium vapor. The vapor shows a sharp maximum absorption exactly at the limit $1s \approx 2414$A and a decreasing absorption toward both shorter and longer wave-lengths. The absorption at longer wave-lengths corresponds to the higher members of the principal series, while that at the shorter wave-lengths is evidence of photo-electric ionization.

The obvious difficulty in the direct determination of the photo-electric effect of vapors by ordinary methods employed for solids arises in the photo-electric emission from the electrodes produced by radiation scattered in the vapor. These electrodes are usually contaminated by the vapor, and since the threshold frequency for the material in the vapor state should be much greater than that for the liquid or solid phases and probably for adsorbed films, a slight contamination completely masks the true photo-electric emission from the vapor. Also, the threshold frequencies of most vapors should be considerably higher than those for electrode materials even when completely free from an alkali metal.

Williamson[3] reduced these difficulties to a minimum by projecting a jet of potassium vapor into a vacuum chamber, and past a carefully diaphramed beam of ultraviolet radiation. The presence of positive ions in the illuminated stream was determined by the use of accelerating and retarding electric fields. Since the amount of ionization produced is extremely small, very sensitive measurements with a Compton electrometer were required, and, in order to obtain high intensity of illumination, a Cooper-Hewitt arc with ultraviolet filters was employed. The ionization with filters cutting off different portions of the ultraviolet indicated that the positive current began somewhere between 2800 and 3100A while $1s$ for potassium corresponds to 2856A. Samuel[4] confirmed this work with measurements of which the following are typical. Current in amperes $\times 10^{-13}$: no illumination .7; illumination 1.7; with filter transmitting to λ2804, 1.5; with filter transmitting to λ2893, 0.7.

Kunz and Williams,[5] using a beam 80A wide from a quartz spectrograph mounted as a monochromator, a quartz arc as source and a three-electrode tube in which the electrodes were exposed to scattered radiation, obtained, by electrometer drifts, an indication of a photo-electric ionization in caesium between 3140 and 3220A. As will be apparent from the results discussed below, the interpretation of the data obtained by these investigators is open to question. If the observed current was not due to

[3] Williamson, Phys. Rev. **21,** 107 (1923).
[4] Samuel, Zeits. f. Physik **29,** 209 (1924).
[5] Kunz and Williams, Phys. Rev. **22,** 465 (1923).

photo-electric emission from the electrodes, it may have been a true photo-electric emission from the vapor excited by the intense 3130 group in the Hg source. Under these circumstances, and provided satisfactory resolving power was employed, spectral energy curves similar to that in Fig. 3 of the present paper should have been obtained. At any rate, an accurate determination of the caesium limit cannot be made with the radiation from a mercury arc since there is very little radiation between 3340 and the intense group at 3130A, while the theoretical limit for caesium is 3184A.

The most recent contribution by Lawrence[6] reopens the entire subject. A method quite similar to Williamson's was employed but much higher precision is claimed and apparently obtained. He concludes that radiation of wave-length greater than 2610A produces no ionization in the jet of potassium vapor while the true photo-electric limit should be 2856A. Lawrence suggests that the effect observed was due to the presence of potassium molecules in the jet. Harrison and Slater, in a paper in this issue, have concluded from an investigation of the absorption spectrum that most of the atoms in rapidly distilling sodium vapor are in molecular

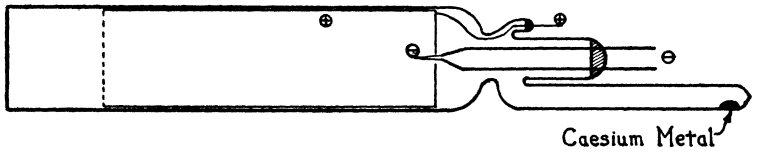

Fig. 1. Tube for measuring photo-ionization by the neutralization of space charge.

combination. If the interpretation of Lawrence be correct the present status of the subject, as far as the direct determination of the photo-electric effect in monatomic vapors is concerned, remains about as described in "The Origin of Spectra."

Description of the Method

In this paper a new method for the measurement of the photo-electric effect in vapors is described which is far more sensitive than any heretofore applied and which is free from difficulties due to scattered radiation. The design of the tube is illustrated in Fig. 1. A small tungsten filament is mounted on the axis of a platinum cylindrical electrode which is closed at the back except for a small hole through which the filament protrudes, and is closed at the front end by a coarse grid. The con-

[6] Lawrence, Abstract in Phys. Rev. **25**, 584 (1925); complete paper to appear in Phil. Mag. The writers express their appreciation for the opportunity of reading this paper in the manuscript.

taining tube is of quartz with a flat quartz window fused to the front and tungsten-glass seals at the back fused in by the use of a quartz-Pyrex graded seal. After thorough baking to remove mercury vapor, caesium metal was distilled in, and the tube was sealed off from the pump. It was then mounted in an oven the temperature of which could be regulated to give the desired vapor pressure. Radiation from various sources such as a concentrated-filament tungsten lamp, mercury arc, etc., was analyzed by a quartz monochromator and directed into the cylindrical enclosure. This was maintained at a potential slightly positive to that of the hot wire. The latter was so operated that the thermionic current was normally limited by the negative space charge, so that the formation of ions by any method tended to neutralize this space charge and permit the flow of more electrons from the wire. Kingdon[7] and Hertz[8] discovered this method independently of each other and applied it for the detection of ions produced by electronic bombardment. However, Kingdon considered the subject in much greater detail and pointed out just why the method is capable of such extreme sensitivity. In general, the ion will possess a tangential velocity component, on account of its thermal agitation. It is repelled by the positively charged outer electrode but like a comet entering our solar system, cannot fall into the negatively charged wire, provided this is of sufficiently small dimensions, since it possesses angular momentum with respect to the wire. In a high vacuum the ion therefore traverses a rosette-shaped orbit about the filament and is imprisoned in the enclosure. When the vapor pressure is increased, the path of the ion is, of course, altered by collision; however, the imprisonment effect still exists. On account of the low mobility of an ion compared to an electron, each trip across the tube neutralizes the space charge of from 100 to 800 electrons, depending upon the vapor. Kingdon actually detected as many as 350 trips so that the high sensitivity of the method is apparent.

Foote and Meggers[9] in 1920 pointed out that a comparatively cool metal surface in the presence of caesium vapor is a copious source of electrons. The explanation of this phenomenon in connection with the work function of the metal is due to Langmuir and Kingdon[10] who have completely developed the theory and use of caesiated filaments. At temperatures below a red heat tungsten in the presence of caesium gives electron currents as high as 0.3 amp./cm^2. The tungsten filament used

[7] Kingdon, Phys. Rev. **21,** 408 (1923).
[8] Hertz, Phys. Zeits. **18,** 307 (1923).
[9] Foote and Meggers, Phil. Mag. **40,** 94 (1920).
[10] Langmuir and Kingdon, Phys. Rev. **21,** 380 and 381 (1923); Science **57,** 58 (1923).

in the present work was about 0.015 cm in diameter and 2 cm long. The saturation current was therefore of the order 28 m-amp., while the current limited by the space charge may be roughly estimated from the equation for the current to a long cylinder from a wire along the axis,[11] as follows:

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{lV^{3/2}}{r\beta^2}=14.68\times10^{-6}\frac{lV^{3/2}}{r\beta^2}\text{ amperes.}$$

Here l is the length of the cathode, r the radius of the cylinder, V the potential in volts and β a complicated function of r/r_0 where r_0 is the radius of the cathode. The quantity β is nearly unity, $l=2$ cm; $r=1.5$ cm so that i at 2 volts is computed to be 5.5×10^{-5} ampere; our observed value was 5×10^{-5}, assuming an initial correction of one volt.

Langmuir and Kingdon have shown that on account of the low ionization potential of caesium and the high work function of tungsten, caesium atoms, evaporated from the filament, leave as positive ions. In order to avoid the neutralization of the space charge by this effect it is essential to operate the filament at as low a temperature as possible. On the other hand the temperature must be sufficient to give a thermonic current which is limited by space charge. There is, accordingly, only a narrow range of filament temperatures over which the tube is a sensitive detector for photo-electric ionization. No difficulty was experienced from this source, but had there been trouble a filament of lower work function might have been utilized.

Since the current without illumination of the vapor is limited by the negative space charge, any ordinary photo-electric emission from the walls or even from the filament itself has no effect.[12] The tube is sensitive only to the presence of positive ions.

Illumination with Unresolved Radiation

A preliminary test of the method was made by the use of the direct radiation from a quartz mercury Labarc, and current-voltage curves were obtained for various filament temperatures and vapor pressures of caesium, both with and without radiation. The increase in thermionic

[11] Langmuir and Blodgett, Phys. Rev. **22**, 347 (1923).

[12] This statement assumes the validity of the simple space charge equation in which initial velocities are neglected. Some of the photo-electrons liberated by quanta of frequency very much higher than the photo-electric threshold of the metal may have velocities sufficient to carry them through the space charge. Under our working conditions this contribution to the observed current was negligible. The total photo-electric current from the cold filament was less than 10^{-8} ampere even with the unresolved radiation from the mercury arc.

current when radiation is directed into the tube becomes greater the higher the vapor pressure and the larger the filament emission. Changes of more than a milli-ampere were observed, and the tube characteristics indicated that much larger effects could be secured under easily realizable experimental conditions.

Fig. 2 shows a group of current-voltage curves with and without radiation and with several filament temperatures. The tube was operated at 135° C, giving a vapor pressure of about 0.007 mm Hg. The section

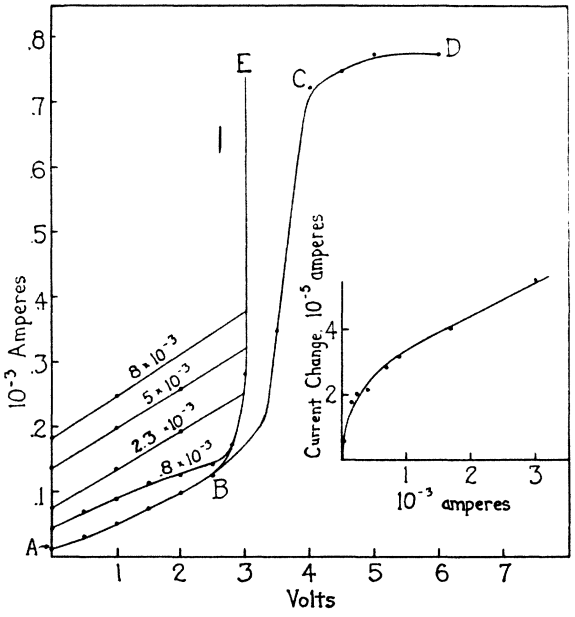

Fig. 2. Current voltage curves in caesium vapor at 135°C. *ABCD* and *ABE* represent thermionic currents for different filament temperatures, without illumination. Curves above *AB* show currents with the vapor illuminated by a mercury arc. Saturation for the filament emission is indicated by the figures over each curve. The inset shows the photo-ionization effect as a function of filament emission.

AB of the lower curve represents the current as limited by space charge without illumination, and was practically the same for all the filament temperatures employed. Near *B* at an applied potential of about 2.7 volts, ionization by electron impact begins. There is an initial potential correction of about 1 volt. The section *BCD* represents the current-voltage relation for only the lowest filament temperature. This current approaches a nearly constant saturation value below 6 volts. At higher temperatures of the filament the current rises more rapidly from *B*, reaching saturation at approximately the same voltage at a point far

above the scale of the drawing. The section BE represents roughly the initial rise for all other filament temperatures. The curves above and approximately parallel to AB were obtained with illumination from the arc, the figures over each curve giving the saturation current above the ionization potential. The *change* in current with radiation is nearly independent of the voltage below the ionization potential but rapidly approaches zero when ionization by electron-impact occurs. The manner in which the *change* in current due to radiation increases with the emissive power of the filament is illustrated by the inset of Fig. 2, which gives the change in current at 1 volt applied potential as a function of the saturation current. The change in current, due to radiation, as a function of the vapor pressure of the caesium, is illustrated by Table I. These values apply for a saturation current of 2×10^{-4} ampere. The actual current at 1 volt, as limited by space charge, was 5×10^{-5}. The ratio of the currents with and without radiation was purposely made small.

TABLE I

Change in current due to radiation as a function of vapor pressure.

Temperature 95°C	Pressure[13] 0.64 bars	Change in current 0.7×10^{-5} ampere
108	1.5	1.1
135	9.7	2.0
145	12.	2.2
170	43.	3.2

For the sensitive detection of radiation the relative change in thermionic current should be as large as possible. The curves in Fig. 2 show that, other conditions remaining constant, the ratio of the currents with and without illumination increases as the potential decreases. The most satisfactory sensitivity was obtained when the outer electrode was slightly less than 1 volt positive to the effective portion of the filament, which in view of the 1 volt initial correction, required a few tenths of a volt negative applied potential. The curves of Fig. 2 show an increase in sensitivity with filament temperature but, as already pointed out, there is a sharp limitation to this relation when an appreciable evaporation of ions occurs. It was found advisable to operate the filament at about 700°C.

MONOCHROMATIC ILLUMINATION

A Hilger ultraviolet monochromator with an aperture ratio of about $f7$ at $\lambda3000$ was employed. Both slits were set at 0.01 inch for most of the work. The caesium tube was heated to 180°C, corresponding to a vapor

[13] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61-79 (1925).

pressure of 0.045 mm Hg. The filament temperature was adjusted for a saturation current of 0.01 ampere and the applied potential was -0.5 volt. When especially high sensitivity was required the thermionic current without illumination, of the order 10^{-6} ampere, was compensated by a potentiometer circuit.

The photo-electric ionization by the mercury arc is shown in Fig. 3. The lower curve gives the increase in current as a function of wave length, in this particular case amounting to 6×10^{-7} ampere at λ3130. Superposed on the curve is a plot of the mercury spectrum. The upper curve gives for comparison radiometric data roughly copied from a

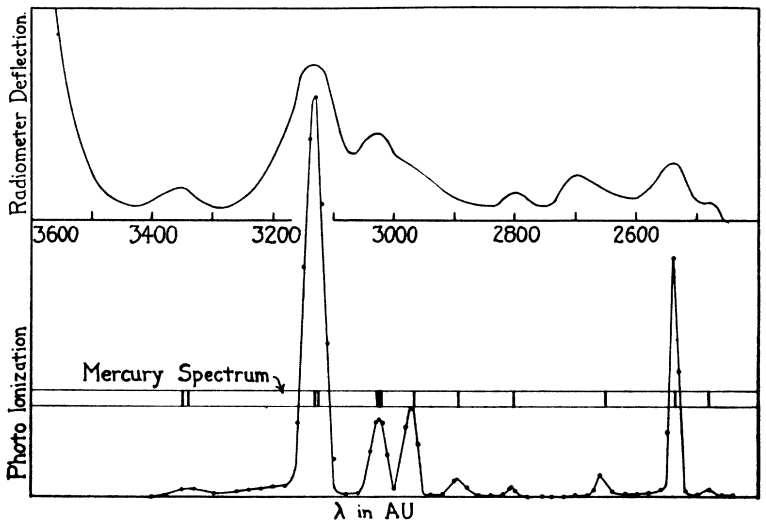

Fig. 3. Lower curve shows change in current with illumination by mercury arc lines as a function of the monochromator setting. Vertical lines superposed on this curve show the positions of the strong arc lines. The upper curve is a rough copy of radiometric data for the mercury arc.

paper by Harrison and Forbes.[14] The two sets of data are, of course, not strictly comparable. The photo-electric ionization is almost zero for wave-lengths greater than 3130 but is well pronounced for this group and for the mercury lines of higher frequency. As already mentioned, the mercury spectrum is deficient in radiation near the 1*s* limit for caesium (λ3184) and hence is not at all a suitable source of radiation for the present requirements. However, the small current observed between λ3130 and 3400 is a true photo-electric effect, as is demonstrated later, and is not due to scattering of radiation by the monochromator.

[14] Harrison and Forbes, J.O.S.A. and R.S.I. **10**, 1-18 (1925).

Curve I of Fig. 4 illustrates the effect observed when a 600 watt glass Mazda lamp was used as a source, the slit width, 0.01 inch, being the same as for Fig. 3. The absorption of the glass is practically complete near 3000A. The energy distribution of this source was roughly estimated by assuming that the tungsten radiated as a gray body at 2700°C and

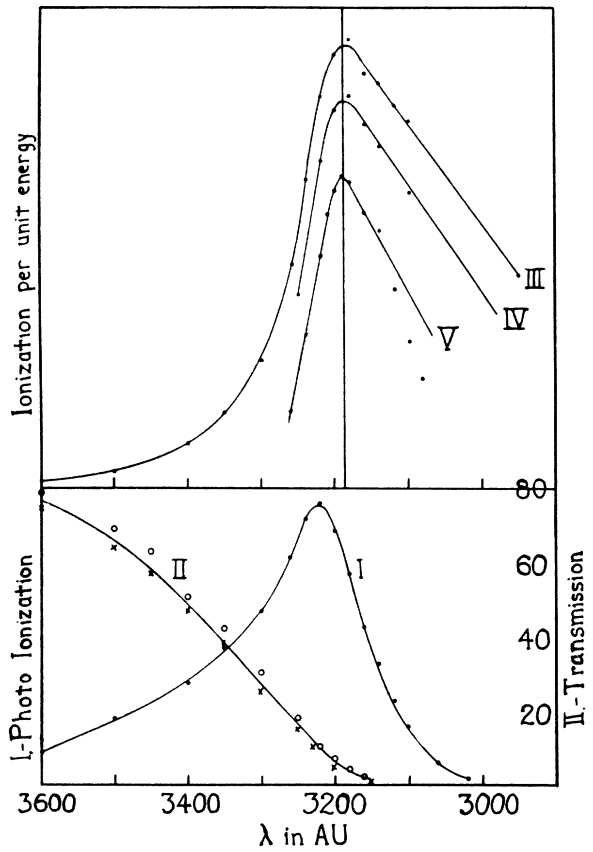

Fig. 4. I. Change in current versus wave-length for illumination by a mazda lamp. II. Transmission of sample of glass; circles determined by photo-ionization; crosses by standard method. III, IV and V. Radiation effect per unit radiation energy. The upper base line is the zero for III.

the values so obtained were corrected by use of spectrophotometric data on the transmission of the glass from a similar lamp. These data were further corrected for the dispersion of the monochromator. Curve III, thus derived from Curve I, shows the radiation effect per unit energy flux from the monochromator, and Curves IV and V represent similar but independent experimental data.

The form of these curves was at first surprising. While the maximum ordinate almost exactly coincides with the limiting frequency 1*s*, the decrease to the left of the maximum is not nearly so rapid as should be expected if there existed for the vapor a sharply defined photo-electric threshold. On the long wave-length side of this threshold value the drop from the maximum should be just as abrupt as for a strong monochromatic line such as λ3130 in Fig. 3.

While Fig. 3 shows no evidence for impurity due to scattering by the monochromator system the following test was made with the mazda lamp as source. The photo-electric ionization effect was measured at various wave-lengths with a sample of glass of known transmission interposed and removed. From these observations the effective transmission coefficient of the glass was obtained. The results of this method are plotted as circles in Curve II of Fig. 4 while transmissions by a standard spectrophotometric method[15] are indicated by crosses. The agreement is quite satisfactory. The transmission at 3184A is less than 5 percent so that scattered light of shorter wave-length would have been almost completely absorbed, thus making our observed transmissions too low. This confirms the existence of a photo-electric effect for the longer wave-lengths and incidentally suggests that the tube employed may prove useful in ultraviolet photometry and intensitometry.

The form of the photo-ionization curve on the short wave-length side is not so certain. The computation of the energy distribution is unreliable near the transmission limit of the glass. The acetylene flame was found too weak for precise measurements although one point at 2950A has been plotted on Curve III. A straight line has been drawn through all the values for wave-lengths less than 3160A, but evidently this linear relation cannot be extrapolated since the sensitivity at 2537 is comparatively high, as shown by Fig. 3.

Interpretation of Results

Curve I of Fig. 5 illustrates the type of absorption observed near an x-ray limit. With high resolving power the edge of the band at the limit is sharply defined and there is satisfactory evidence that the energy absorbed is expended in ionization in the manner required by the Einstein photo-electric equation. Curve II illustrates the type of absorption observed near the limit 1*s* of the principal series of an alkali vapor. This is a schematic adaptation for caesium of data for sodium by Harrison.[16]

[15] These measurements were made by Dr. K. S. Gibson of the Colorimetry Section, Bureau of Standards.

[16] Harrison, Phys. Rev **24,** 466-77 (1924).

The unresolved line absorption on the long wave-length side merges into the continuous absorption beyond the limit so that the general appearance of the curve is quite different from that obtained in the x-ray region. Interpreted on the basis of Bohr's theory, the absorbed energy of frequency higher than the limit 1*s* produces ions; the absorption of lower frequencies produces atoms in various states of excitation. These

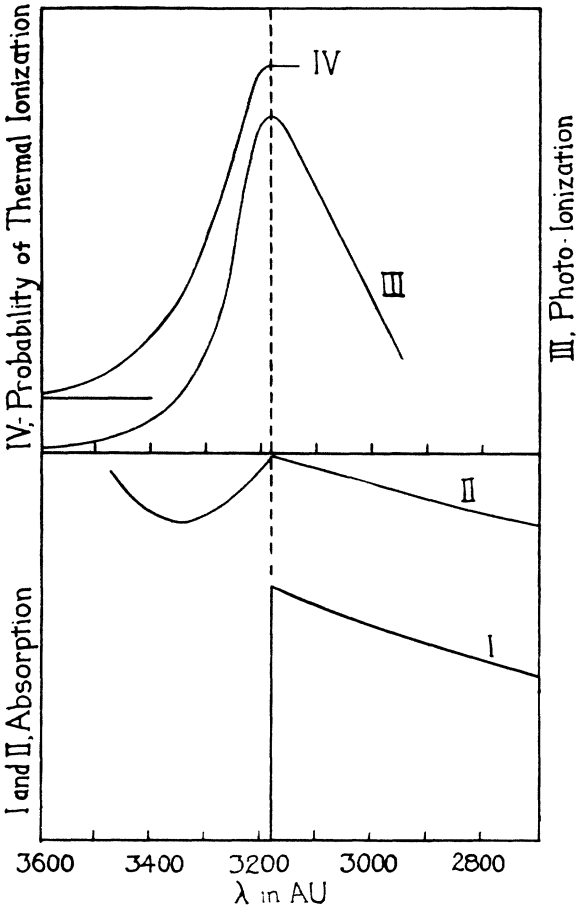

Fig. 5. I. Variation of absorption with wave-length near x-ray limit. II. Absorption near 1*s* limit of an alkali vapor. III. Photo-ionization effect. IV. Probability of ionization from an *mp* state by atomic collision at 180°C as a function of wave-length 1*s*—*mp*.

latter being neutral should not be detected by the present method of analysis so that unless some secondary process occurs, the drop in the photo-ionization curve should be abrupt as in the case of an x-ray limit.

The secondary phenomenon effective is the ionization by collision of excited atoms.

At the temperatures and pressures employed in this experiment the average duration of the mean free path of a normal caesium atom is comparable with the life of an atom in an excited state.[17] Since the size of an atom rapidly increases for the higher stages of excitation, the mean period becomes smaller, and in general an excited atom will collide with another atom before it has had time to radiate. The relative kinetic energy of the two colliding atoms may suffice to complete the process of ionization. Thus, a collision at the r.m.s. speed for 180°C involves kinetic energy sufficient to ionize a caesium atom in the $15p$ state, a state which is produced by the absorption of 3231A, nearly 50A beyond the proper threshold value. From simple kinetic theory, the fraction F of the total number of collisions in which the translational energy of one atom relative to the other is greater than E_0 ergs has the form

$$F = [1+(3.64/T)E_0 \cdot 10^{15}]e^{-(3.64/T)E_0 10^{15}}.$$

If E_0 represents the work required to ionize a caesium atom from an excited p state, one finds, for example, that 93 percent of the collisions at 180°C may produce ionization from the $20p$ state, the latter condition following the absorption of λ3210. Similarly, 30 percent of the collisions may effect ionization from the $8p$ level, this state following absorption of λ3348. Curve IV of Fig. 5 shows the fraction F plotted against the wave-length $1s$—mp. It therefore represents a controlling factor in the probability of ionization from an mp state produced by absorption of the radiation $1s$—mp. This incomplete probability function has almost exactly the same form as the observed photo-ionization data, Curve III. The two graphs have been displaced vertically to avoid confusion. The quantitative agreement is fortuitous, since several factors entering into the exact form of the probability curve have not been considered; for example, the absorption coefficient of the vapor, the life and the mean free path or time of an excited atom. However, the computations show at least qualitatively that interatomic collisions can account for the observed ionization on the long wave-length side of the threshold.

These considerations show that the setting in of ionization whether by radiation or by electron impact cannot be sharply discontinuous under any effective experimental conditions. Much lower pressure, and resulting decrease in sensitivity, may make ionization by interatomic collision inappreciable, but even then photo-ionization by infrared radia-

[17] Estimated as 1.4×10^{-8} sec. for sodium; cf. Ellett, J.O.S.A. and R.S.I. **10**, 437 (1925).

tion may play an important rôle. The radiation corresponding to the maximum intensity from a black body at 180°C has a frequency sufficient to ionize a caesium atom from the $8p$ state.

An investigation of the relative importance of the ionization of excited atoms by heat radiation and by interatomic collision will require data similar to Fig. 4 for various pressures and temperatures. It is important to investigate the exact form of the photo-ionization curve on each side of the maximum. Possibly with higher resolution the curve on the long wave-length side will show secondary peaks corresponding to the successive members of the principal series. It is evident that the general method described is applicable to many problems in cumulative ionization.

In conclusion, the writers desire to thank Dr. Sebastian Karrer of the Fixed Nitrogen Laboratory for the loan of the quartz monochromator and Mr. R. L. Chenault for assistance in making the observations.

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