RECOMBINATION SPECTRA OF IONS AND ELECTRONS IN CÆSIUM AND HELIUM

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ABSTRACT

Method.—Thermionic discharges in cæsium and helium were operated to give strong continuous bands and spectrophotometer measurements of intensity distribution were made in connection with probe wire measurements of electrical conditions.

Discharge Conditions.—Excitation of these spectra is favored by high electron and ion concentrations of the order 10^{13} per cc and low electron speed. Electrons have a Maxwell distribution of average energy between 0.15 and 0.4 volt.

Intensity.—Intensity depends on the ion concentration independent of discharge current and voltage. The increase with ion current is less than the square and nearly the first power at high intensity. Intensity increases rapidly with pressure.

Intensity Distribution.—Measurements of intensity distribution in the 2 P band of cæsium and of electron velocity distribution were made under a variety of discharge conditions. Some measurements on the 3 D band are given. Photographs and approximate intensity measurements on continuous bands of helium show a strong band beyond $2\,^3P$ and fainter bands beyond $2\,^3S$, $2\,^1P$, and $2\,^1S$.

Afterglow.—By means of a sectored disk and commutator the spectrum of the cæsium afterglow was photographed. It is characterized by a more rapid decrease in intensity of the continuous bands with decreasing wave length.

Conclusions.—Results on intensity distribution are explained on the basis of simple recombination, although absolute values can not be explained in detail. The relative values of probability of recombination as a function of electron energy are independent of discharge conditions. The form of the functions for the levels 2 P and 3 D of cæsium are similar. The probability of recombination is proportional to $1/\nu^2\sqrt{\nu-\nu_i}$. This corresponds by the principle of detailed balance to an absorption coefficient beyond the limit proportional to λ^4.

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I. INTRODUCTION

Another paper of the same title[1] describes a type of thermionic discharge in cæsium which shows strong continuous spectra extending to the violet from each series limit. The intensity of the continous bands was enhanced with increased current and vapor pressure in a manner consistent with the hypothesis that the radiation resulted from recombination. The paper included photographs of the spectra in potassium as well as cæsium and visual spectrophotometer measurements of the cæsium bands.

The present paper describes experiments in which probe wire measurements of electrical conditions in the discharge were made in connection with intensity measurements. It includes measurements in cæsium and in helium.

When an electron of velocity v recombines with an ion into an energy level of limiting frequency ν_1, it will radiate a quantum of frequency ν where

$$h\nu = h\nu_1 + \tfrac{1}{2}mv^2 \tag{1}$$

Thus, the intensity $J(\nu)$ at any frequency greater than ν_1 depends on the concentration of electrons of the corresponding speed, $N^-(v)$ on the concentration of ions, N^+, and on a probability factor which is a purely atomic property. The probability can be expressed as the effective collision area times the electron velocity $vq(v\nu_1)$. Equating the quanta emitted and the effective collisions

$$J(\nu)/h\nu\, d\nu = \Sigma N^-(v) \cdot N^+ \cdot vq(v\nu_1)\, dv \tag{2}$$

The summation extends over all limits of frequency less than ν, but in practice one level is usually predominant at any one frequency.

Unfortunately, inherent difficulties in the electrical measurements leave the values of the concentrations uncertain, so that only relative values of $q(v\nu_1)$ are derived. There is a possibility that under the experimental conditions the random Stark effect of neighboring ions will seriously alter the values of this. A recent theoretical paper on Stark Effect and Series Limits[2] discusses the results obtained in the earlier paper[3] and shows that the limits of separate atoms may be diffused over a range of several hundred angstroms. Paschen[4] has made use of the Stark effect broadening of lines to estimate the ion concentration in helium discharges showing recombination bands.

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[1] F. L. Mohler, Phys. Rev., **31**, p. 187; 1928.
[2] Robertson and Dewey, Phys. Rev., **31**, p. 973; 1928.
[3] See footnote 1.
[4] Paschen, Berlin Ber., p. 135; 1926.

II. APPARATUS AND PROCEDURE

1. DISCHARGE TUBES

Most of the work has been done with a quartz tube with a flat window at one end. A hot wire cathode (either tungsten or oxide coated platinum) was near the axis of a cylindrical anode with the ends closed except for slits for viewing the discharge. The probe was usually a platinum wire 4 to 10 mm in length and 0.5 mm in diameter, placed parallel to the axis within a centimeter of the cathode. In a general survey of discharge conditions a variety of probes have been tried, and in one tube the probe could be moved by an external magnet.

The cæsium tubes were sealed off the pumps after outgassing, while in work with helium the gas was either circulated through charcoal in liquid air or at least kept in contact with the charcoal trap during the experiment.

2. INTENSITY MEASUREMENTS

A method described in the first paper has been adapted to photographic spectrophotometry. A region of the discharge close to the probe was focused on the plane of the filament of an incandescent lamp, and this was focused on the slit of the spectrograph. Quartz fluorite achromats were used and the lamp was a quartz tube with flat end plates containing a tungsten hairpin filament. This was calibrated in terms of color temperature versus current by an optical pyrometer. The procedure was to match the filament and discharge visually or by trial and then take a series of exposures, changing the lamp current by convenient steps. The photographs showed the wave lengths at which a match was obtained, and the intensity at these wave lengths could be computed by Wien's law.

In some work the intensity of the cæsium 2 P band was measured by sighting an optical pyrometer with a green glass in the eyepiece directly on the discharge. The glass transmitted a narrow spectrum range near the head of this band.

3. ELECTRICAL MEASUREMENTS

The usual method of measuring probe characteristics was used except that because of the rapid variation in current it was necessary to correct the applied potential for the voltage drop across the leads and milliammeter. Voltages were measured relative to the anode.

The theory developed by Mott-Smith and Langmuir [5] has been applied. At negative potentials such that only positive ions reach the probe the current I^+ is given by the equation

$$I^+ = N^+ ea\sqrt{eV_0^+/3\pi M} \qquad (3)$$

[5] Mott-Smith and Langmuir, Phys. Rev., 28, p. 727; 1926.

where N^+ is the concentration, V_o^+ the average kinetic energy, and M the mass of the ions; a is the area of the sheath around the wire and changes with the voltage in accord with the space charge equation. On the basis of published tables, a can be evaluated from the value of I^+ at any applied potential V.[6]

As the negative potential is reduced, electrons reach the probe and, in general, these fall in several velocity groups, the slowest of these groups being by far the largest. Assuming that this group has a Maxwell distribution, the current contributed by it is:

$$I^- = a_o N^- e \sqrt{eV_o/3\pi m}\ \epsilon^{-3V/2V_o} \tag{4}$$

$$\log I_2 - \log I_1 = 3/2 \log \epsilon\ (V_1 - V_2)/V_o \tag{5}$$

where N^- is the concentration and V_o is the average energy of the electrons; a_o is the area of the probe, while V_1, V_2, I_1, I_2 are specific values of V and I. The plot of log I against V is a straight line, if there is a Maxwell distribution, and the slope of this determines V_o. The linear relation ends at $V=o$, and the coordinates of this discontinuity give the space potential and N^-. Note that V_o^+ of (3) is not measured and N^+ is not directly determined.

III. GENERAL REMARKS ON DISCHARGE CONDITIONS

The continuous spectra were excited in cæsium with currents between 0.1 and 1.5 amps., applied potentials between 2 and 10 volts, and a vapor pressure of 0.05 mm or more. In helium comparable currents were used at from 20 to 50 volts with a pressure between 2 and 15 mm. Under these conditions the potential drop is concentrated in a thin sheath around the cathode, while a diffuse glow extending toward the anode shows the continuous bands. The region of diffuse glow is characterized by high ion concentration and extremely low electron speed. Semilog plots of the electron current are linear, which indicates that most of the electrons fall in a single group with a Maxwellian distribution. The average energy is between 0.1 and 0.4 volts. Attempts to extend the current voltage curves through the space potential were generally unsuccessful. Except with extremely small probes the probe current robs the discharge before the space potential is reached. With small probes the currents tend to drift and become unsteady, presumably because of overheating.

Results obtained with larger probes permit accurate determinations of the average electron energy and the positive ion current, and it has seemed advisable to limit our attention to these measurements for the present rather than to sacrifice precision.

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[6] Langmuir and Blodgett, Phys. Rev., **22**, p. 347; 1923.

The change in positive ion current with voltage was relatively small and could be accounted for by the space charge equation. In some cases a well-defined group of high-speed electrons was detected with a maximum energy of 10 to 15 volts in helium and of 2 to 3 volts in cæsium.

In spite of the incomplete data some estimate can be made of the space potential N^+ and N^-. In the highly ionized force-free space N^+ and N^- must be nearly equal. The average energy of the ions, V_0^+, will be intermediate between that of the gas atoms and that of the electrons, in an average case between 0.07 and 0.2 volt. This gives an uncertainty of about twofold in the value of N^+ in equation (3), and I^- at the space potential can be computed with the same uncertainty assuming $N^- = N^+$. The linear semilog plot can be extrapolated to this value of I^-, and as the electron current doubles in a range of about a tenth of a volt the space potential is determined with an uncertainty of less than 0.2 volt. Measurements with a movable probe in a cæsium discharge of 0.3 amp. at 5 volts gave the following results: At 6 mm from the cathode the average electron energy V_0 was 0.35 volt, and assuming an ion velocity corresponding to 1,000° K., N^+ was 1.5×10^{13} per cc. The space potential V_s was about $+1.3$ volts relative to the anode. Close to the anode $V_0 = 0.22$ volt, $N^+ = 1.3 \times 10^{11}$ and $V_s = +0.4$. With a discharge of 0.1 amp. at 6 mm from the cathode, $V_0 = 0.22$ volt, $N^+ = 0.4 \times 10^{13}$ and $V_s = +1.0$, while near the anode $V_0 = 0.19$ volt, $N^+ = 0.27 \times 10^{11}$ and $V_s = +0.2$. In general, V_0 increases near the cathode and increases as the ion concentration increases. Because of the slightly positive space potential, ions diffuse to the anode as well as to the cathode, while slow electrons are to some extent imprisoned in the space.

IV. INTENSITY AND DISCHARGE CONDITIONS

1. INTENSITY

Measurements covering a wide range of current and voltage were made by sighting the optical pyrometer, with a green glass in the eyepiece, directly at a cæsium discharge. Figure 1 gives a plot of the measurements of intensity against ion current, I^+, at a vapor pressure of 0.25 mm. The intensity seems to increase nearly linearly beyond the current range of Figure 1, but the probe measurements become unreliable. The plot shows that within the limits of experimental error the intensity is determined by I^+ and is independent of the particular discharge current and voltage used to give I^+. Spectrophotometer measurements in cæsium and helium are in agreement with these results. In helium, as in cæsium, the variation of intensity is much less than the square of the current and at least at the higher intensities is nearly proportional to the first power.

The intensity increases rapidly with the pressure for both cæsium and helium. The relation has not been studied quantitatively, but exposures at 2, 3, and 4 mm of helium show an intensity ratio of roughly 1 to 4 to 8.

2. INTENSITY DISTRIBUTION

It follows from equation (2) that on the basis of measurements of electron velocity distribution and intensity distribution in a continu-

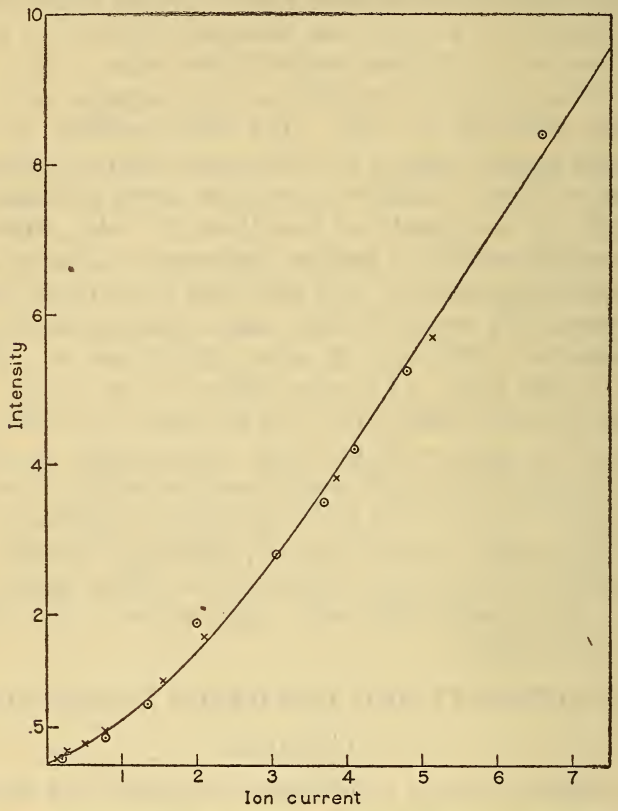

FIG. 1.—*Intensity near 2 P limit of cæsium versus ion current to probe*

Crosses show measurements with discharges at 5 volts and currents between 0.015 and 0.2 amp. Circles give measurements at voltages between 7.8 and 1.5.

ous band one can derive relative values of the probability of recombination as a function of the electron velocity. The 2 *P* band of cæsium falls in a convenient region for intensity measurements and has been studied most carefully.

A set of photographs and visual intensity matches combined with probe wire measurements were made under constant discharge conditions. The ion current was kept constant by slight variations in

the discharge current or voltage. The chief experimental difficulty was the variation in vapor pressure during the series of exposures which usually required about six hours.

Figures 2 to 4 show two sets of data on electron current, intensity distribution, and probability of recombination obtained under different conditions. For set *I* the cæsium temperature was 190° C., and the discharge was operated at about 7 volts and 0.9 amp. to give an ion current of 14 m. a. and an ion concentration of roughly 8×10^{13} per cc. For set *II* the cæsium temperature was 198° C., discharge voltage 4 volts, current 0.55 amp., ion current 1.4 m. a., and concentration 0.8×10^{13}. Figure 2 is a semilog plot of the electron currents against the voltage for the two cases, and it shows that there is a strictly Maxwell distribution about an average energy of 0.345 volt for set *I* and 0.281 volt for set *II*. Figure 3 is a semilog plot of intensity as a function of wave length. This method of plotting was chosen as the most convenient for interpolation. The difference in form of the two curves is rather small but well beyond the probable error. Dividing the number of quanta at a given wave length by the relative number of electrons at the corresponding speed and multiplying by λ^2/v to transform to proper variables gives a number proportional to $v\ q\ (v,\ 2\ P)$. Figure 4 shows the two sets of computed values reduced to the same scale by a single arbitrary constant. Six other sets of data have been obtained, and the resulting $v\ q\ (v)$ values fall close to this curve, although the precision was not always as good as in the cases illustrated. The average electron energy varied from 0.28 to 0.38 volt while the ion concentration ranged from 0.8 to 15×10^{13}.

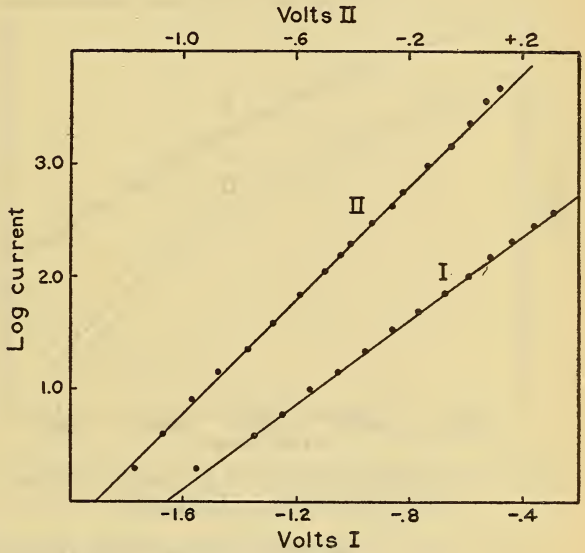

FIG. 2.—*Electron velocity distribution curves*
I gives $V_0 = 0.345$ volt; *II* gives $V_0 = 0.281$ volt

Visual spectrophotometer measurements have been made on the 3 *D* band, together with measurements of electron velocity. Similar

intensity measurements are illustrated in the first paper.[7] Line spectra and the 2 P band seriously limit the range and precision of the measurements. These data are included in Figure 6.

The spectrograms of the helium discharge closely resemble published photographs by Paschen[8] of the spectrum of the hollow cathode discharge. Continuous bands can be detected beyond the limits 2 ^1P, 2 ^3P, 2 ^1S, and 2 ^3S though the 2 ^1P band is obscured by molecular bands and the 2 ^1S band is masked by the stronger 2 ^3P band. The degree of purity of the gas is an important factor. A trace of mercury suppresses the helium molecular bands and facilitates observation of the continuous bands, but traces of other common impurities mask the continuous bands completely. Figure 5 is a plot of the intensity distribution based on spectrophotometer measurements. The estimates of intensity on the red side of 2 ^3P and on the violet side of 2 ^3S are extremely uncertain. The discharge conditions for this set of measurements were pressure 4 mm, discharge at 50 volts and 0.5 amp., average electron energy 0.25 volt, ion concentration 10.[13]

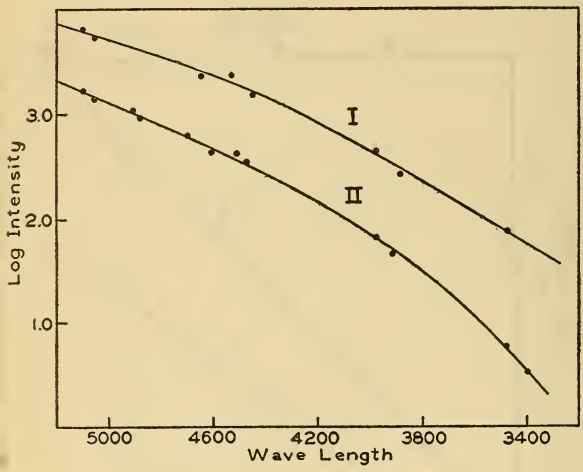

FIG. 3.—*Intensity distribution in 2 P band of cæsium*

I for V_0=0.345 volt; *II* for V_0=0.281 volt

3. AFTERGLOW OF THE DISCHARGE

A sectored disk and commutator were arranged so as to cut off the discharge and permit study of the spectrum of the afterglow. Only qualitative results have been obtained so far. An exposure to the cæsium afterglow was made with a discharge of one ampere and disk speed of 1,500 r. p. m., giving a time interval of about 10^{-3} second between cutting off the discharge and uncovering the spectroscope slit. Comparison exposures on the direct discharge were made on the same plate. Higher series lines are somewhat stronger in the afterglow as was found by Miss Hayner in her study of the mercury afterglow,[9] but the contrast is less marked in this case as the recombination radiation is predominant even in the direct discharge. For the same reason recombination intensity does not reach a maximum

[7] See footnote 1, p. 490. [8] See footnote 4, p. 490. [9] Hayner, Zeits. f. Phys., 35, p. 356; 1926.

after the cut-off but seems to fade continuously. The most striking difference between the discharge and afterglow is that the continuous bands fade toward the violet much more rapidly. The intensity at 4,700 A, relative to that at the 2 *P* limit, is about half as great as in the spectrum of the direct discharge. This can be explained on the basis of electron velocity, which will quickly drop after the discharge is cut off. Assuming that the average electron energy in the discharge is 0.3 volt (2,300° K.), we estimate from the intensity change that the electron energy or temperature in the afterglow is roughly 0.1 volt, or 800° K. As there will be 10^6 electron collisions in 10^{-3}

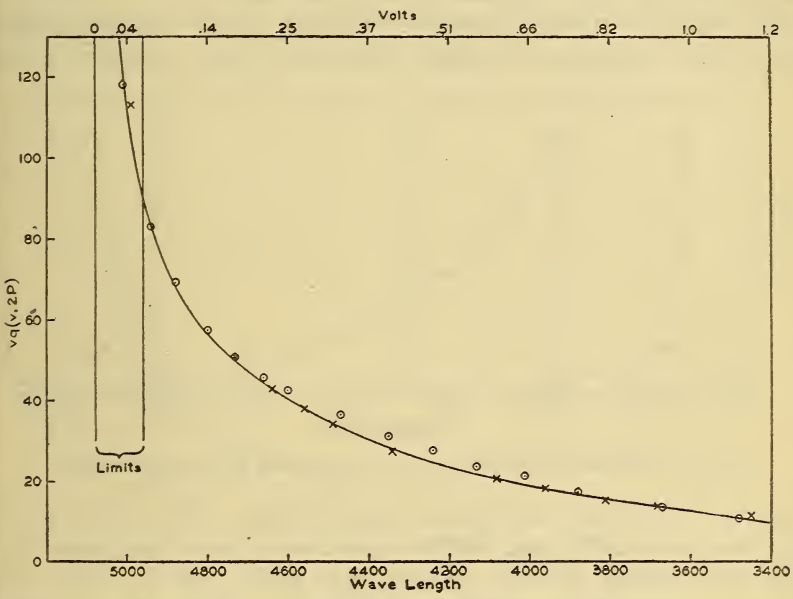

FIG. 4.—*The relative probability of recombination into 2 P from data of Figures 2 and 3*

Crosses refer to set *I* and circles to set *II*. Abscisas are in wave lengths below and corresponding voltage values above

seconds, it is not surprising that electrons have nearly reached equilibrium with the gas at 500° K.

V. DISCUSSION

The relation between intensity and ion current as illustrated in Figure 1, as well as the increase of intensity with pressure, can not as yet be satisfactorily explained. On the basis of the simplifying assumptions which were introduced in the discussion of discharge conditions, one would predict from equation (2) that the intensity should increase as the square of the ion current and be independent of the pressure. The observed increase is much less than the square. Thus, in Figure 1 the highest observed intensity is about a fifth of the com-

puted value.[10] The assumptions may well introduce an uncertainty of the order of twofold but there remains an unexplained discrepancy. As regards the effect of pressure, presumably the ion concentration is increased by the combined effect of lower ion temperature and changed probe characteristics, but this can scarcely account for the magnitude of the intensity change. Franck has proposed the theory that an atom may recombine in the process of ionization by collision [11] with the emission of continuous radiation. The intensity in this case would depend only on the number of collisions with high-speed electrons. We could find no correlation between the intensity and the presence of such electrons in our experiments.

The relation between intensity distribution and velocity distribution of slow electrons is entirely consistent with equation (2) and

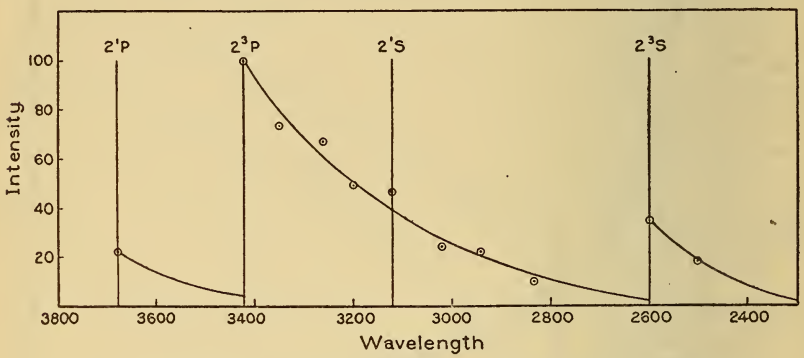

FIG. 5.—*Intensity distribution in the continuous spectrum of helium*

supports the theory of simple recombination. The form of the function $v\ q\ (v,\ 2\ P)$ was, within experimental error, the same for a range of average electron energy from 0.281 volt to 0.375 volt. (Electron temperature 2,180° to 2,900° K.) It is also significant that the form of the $v\ q\ (v)$ curve is independent of the ion concentration which varied from 0.8×10^{13} to 15×10^{13}. We conclude that the influence of random Stark effect on the intensity distribution is not a serious source of error. The experimental conditions also covered quite a range of pressure and discharge voltage.

There is a general relation based on the principle of detailed balance between the probability of recombination $v\ q\ (v\ \nu_1)$ and the probability of absorption $B\ (\nu\ \nu_1)$ at the frequency ν corresponding to V.[12]

$$v\ q\ (v\ \nu_1) = K_1\ B\ \cdot\ \nu^3/\sqrt{\nu - \nu_1} \qquad (6)$$

The B, of course, applies to atoms initially in the state ν_1 and is quite unmeasurable except where this is the normal state. In the X-ray

[10] Later measurements with a spectrophotometer show that at low currents the intensity is proportional to the square of the current and the lower portion of the curve of Figure 1 is inaccurate.

[11] Franck, Zeits. f. Phys., **47**, p. 509; 1928.

[12] Milne, Phil. Mag., **47**, p. 209; 1924.

range B is proportional to ν^{-4}, and theoretical derivations show that in hydrogenic atoms it will approximate to the same law. Oppenheimer [13] finds by the methods of wave mechanics that the value of the exponent for atomic hydrogen varies from -4.3 at the limit to a minimum value of -3.5 for the normal level, and other levels vary slightly from this. The ν^{-4} absorption law in equation (6) gives:

$$v\,q(v) = K_2/\nu\sqrt{\nu-\nu_1} \tag{7}$$

He [14] has also derived the relation that $v\,q\,(v)$ is proportional to $(\nu-\nu_1)^{-3/2}$ near the limit. This result and his absorption law are not consistent with equation (6).

Direct measures of B for the continuous bands beyond absorption series limits are apparently invalidated by superposed molecular

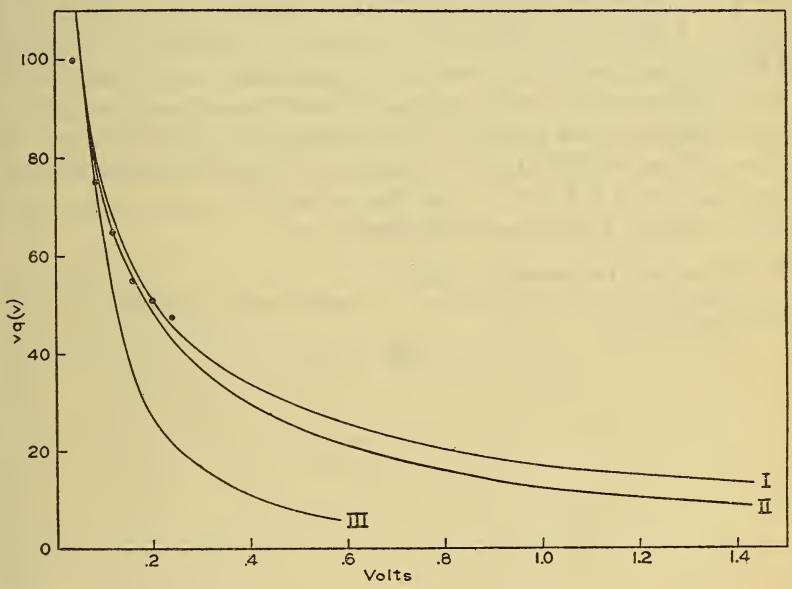

FIG. 6.—*Relative probability of recombination*

I, Theoretical curve derived from ν^{-4} law for B
II, $v\,q\,(v\,2\,P)$ from Figure 4. Dots $v\,q\,(v\,3\,D)$
III, $v\,q\,(v, 1\,S)$ derived from photoionization measurements

absorption,[15] but measurements of photoionization may be free from this objection and independent measurements on the 1 S band of cæsium are in satisfactory agreement.[16] [17] The curve of Figure 4 is drawn according to the equation

$$vq\,(v,\,2\,P) = K/\nu^2\sqrt{\nu-\nu_1} \tag{8}$$

[13] Oppenheimer, Zeits. f. Phys., **41**, p. 268; 1927.
[14] Oppenheimer, Phys. Rev., **31**, p. 349; 1928.
[15] Harrison and Slater, Phys. Rev., **26**, p. 176; 1925.
[16] Mohler, Foote and Chenault, Phys. Rev., **28**, p. 37; 1926.
[17] Little, Phys. Rev., **30**, p. 109; 1927.

which fits the observations exactly. This gives B proportional to ν^{-5}, and the absorption coefficient varies as ν^{-4} or λ^4. The factor $\sqrt{\nu-\nu_1}$ is predominant in giving the shape of the curve, so that the power of ν is not determined with precision. In Figure 6, *II* is the curve of Figure 4, while *I* is derived from the ν^{-4} law for B. The difference is probably greater than the experimental error. The dots in Figure 6 are derived from the less accurate intensity measurements on the 3 *D* band. Curve *III* is derived from observed values of photoionization,[18] and there is a serious discrepancy between this and Curve *II* which can not be explained. The $V^{-3/2}$ law of Oppenheimer gives a curve much steeper than *III*.

Curve *II* of Figure 6 shows that the probability of recombination increases very rapidly as the electron energy decreases below 0.3 volt, while above 0.5 volt the probability is small, and the rate of change is small. A figure for the absolute value of the probability is of little significance because of the discrepancy mentioned above, but the data of set *II*, Figures 2, 3, and 4, give a value of the order of 2×10^{-19} cm^2 for the effective cross section for recombination into 2 *P* at 0.2 volt. This would mean that about 1 collision in 5,000 would result in such recombination at 0.2 volt. The chance would be four times as great at 0.05 volt and a third as much at 0.5 volt.

WASHINGTON, October 30, 1928.

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[18] See footnote 16, p. 499.