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PHOTO-IONIZATION AND RELATIVE ABSORPTION PROBABILITIES OF CAESIUM VAPOR*

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ABSTRACT

Measurement of photo-electric ionization in gases.—The method[1] depends upon the partial neutralization of the negative space charge around a hot wire cathode by the ions produced by radiation. The change in thermionic current is proportional to the product of the intensity of radiation, number of atoms of vapor per unit volume, the Einstein probability coefficient B_ν, a quantity R representing the number of electrons released by a single ion and certain numerical factors relating to the geometry of the apparatus. The magnitude of R is of the order 10^4 to 10^6 depending upon the vapor pressure and other characteristics of the tube. Under constant experimental conditions and when the change in current upon illumination is small compared to the total thermionic current, R assumes a definite fixed value. Hence the change in current per unit intensity at different frequencies gives relative values of B_ν.

Absorption probabilities.—The absorption probability coefficient of a caesium atom for wave-lengths shorter than the $1s$ limit λ3184 decreases much more rapidly with decreasing wave-length than follows from the λ^3 law of Milne or the λ^4 law of Kramers although the latter is satisfactory for x-ray absorption. The theory of Becker is in good agreement with the data for the range λ3050 to 2700. An empirical relation of the form $B_\nu = B_{\nu_1} e^{-a(\lambda_1-\lambda)}$ where $\lambda_1 = 3184$, appears to represent the experimental values throughout the observed range λ3184 to 2600. Vapor pressures investigated extended from 5 to 500 bars.

Photo-excitation.—Photosensitivity curves between λ3900 and the limit show that appreciable ionization is produced only at the wave-lengths corresponding to the principal series lines, the resolved effect of the individual lines being measurable from $1s-4p$ to $1s-9p$ with indications of further peaks, the definition of which was limited by the resolving power of the monochromator. The ionization is due to the production of excited atoms which are ionized by atomic collision. The relative magnitude of the photo-ionization at the different lines is in accord with the theory based upon the above hypothesis.

RECENTLY[1] two of the authors described a new method for detecting the photo-electric ionization of a gas, which was applied to the measurement of the photo-electric effect in caesium vapor. The vapor was contained in a two-electrode quartz tube. A hot wire cathode was enclosed by a cylindrical electrode having a gauze end through which the exciting radiation was transmitted. Conditions were adjusted to be

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

[1] Foote and Mohler, Phys. Rev. **26**, 195-207 (1925).

such that the electron current without illumination was limited by space charge and the formation of ions by the radiation tended to break down the space charge and to produce an increase in thermionic current. This effect is greatly accentuated by the imprisonment of the ions, as a result of which a single ion may be responsible for the emission of 10^5 or more electrons. The photo-ionization of caesium vapor was found to be a maximum at the limit of the principal series, λ3184. Photosensitivity was also observed at longer wave-lengths which was attributed to the ionization by interatomic collision of excited atoms.

The present paper is a continuation of this work. The tube was operated at temperatures ranging from 130 to 230°C. With an applied voltage greater than the ionization potential, a current of about 10^{-2} amp. was obtained. As indicated by the voltage at which ionization occurred the actual potential difference was about 1 volt greater than the applied value. For the photo-ionization measurements the applied voltage was zero, and the current was 2×10^{-5} amp. which agrees with the value computed from the space charge equation when $V=1$ volt. The thermionic current was balanced out by a potentiometric circuit, and the galvanometer sensitivity was increased as desired for the radiation measurements. Under favorable conditions a sensitivity as high as 4×10^{-10} amp. per mm could be utilized. The increase in current due to the illumination, if small compared to the total thermionic emission, is proportional to the number of ions formed. With the potentiometric circuit, this increase in current is read directly from the galvanometer deflection.

The amalgam mirror of the Hilger quartz monochromator (aperture $F/7$ at λ3000) was replaced by a sputtered platinum surface, the reflection coefficient of which is known. As light sources were used a 400 watt concentrated filament Mazda lamp, a quartz mercury arc and a tungsten lamp with a quartz window, containing mercury vapor to suppress volatilization of the filament. The sources were focused on the entrance slit of the monochromator while no lens was employed between the exit slit and the ionization tube.

Galvanometer drift and slight changes in photosensitivity of the tube, in part due to temperature variation, were greatly reduced by using storage batteries for all the electrical circuits and by adjusting the currents several hours before obtaining the final measurements. Three galvanometer readings were observed at each monochromator setting, with the illumination on, off and on; a series of such measurements were made for a range of wave-lengths and then repeated in the reverse order. In general, slit widths of 0.005 inch were used with the Mazda lamp in the range λ3900 to 3100 while slits as wide as .04 inch were necessary with the quartz tungsten lamp at the shorter wave-lengths near λ2800.

Data showing the relative values of the ratio of photo-electric ionization to light intensity as a function of the wave-length are of especial interest in connection with the theoretical interpretation of ionization by radiation. Unfortunately the intensity of the radiation incident upon the ionization tube was insufficient for a direct evaluation by means of a thermopile. Dr. Coblentz very kindly made several thermopile measurements for us with the mercury arc as source, but only two or three of the strongest ultraviolet lines could be detected with certainty and the galvanometer deflections for these were less than 1 cm. Intensity values were therefore obtained by computation using the thermopile data merely as a check.

The radiation flux $J_\lambda \Delta\lambda$ with the tungsten-quartz lamp as source was assumed proportional to the intensity of a gray body at 3000°K, times the reflecting power of the platinum mirror, times the reciprocal of the dispersion factor of the monochromator. With the Mazda lamp, these values were further multiplied by the transmission coefficients of a sample of glass from a similar lamp.

EXPERIMENTAL DATA

Table I illustrates the experimental conditions under which the photo-ionization measurements have been made. The vapor pressures are computed from data by Langmuir and Kingdon.[2] At the four higher temperatures both tungsten lamps were employed and in the range λ3600 to 3100 readings were made with a 0.005 inch slit at 10A intervals. The Mazda lamp alone was used at the lower temperatures and fewer measurements were obtained.

TABLE I

Conditions for photo-ionization measurements
(Mazda lamp illumination)

Temp.	Pressure	Current at 3200A slit .01 inch	slit .005 inch
230°C	500 bars	19.5×10^{-8}amp.	4.7×10^{-8}amp.
202	170	24.2	5.7
182	74	....	2.9
162	29	9.0	2.2
149	15	6.7	...
134	9.7	4.2	...
128	5.0	1.6	...

Fig. 1 shows the photosensitivity, corrected for an equal energy spectrum, as a function of the wave-length, for the temperatures 182° and

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

230°C. Table II gives some of the data for these curves as well as the relative values of the incident radiation flux. The last two columns tabulate the heights of the separate peaks in the curves of Fig. 1 from λ3880 to 3310 and the points on the continuous curve for shorter wave-lengths. These values are the directly determined means of the experimental data. There is a small but perceptible difference between the two curves of Fig. 1. Curves for 162° and 202° resemble closely that for 182°, as do also the less accurate data for the lower temperatures.

TABLE II

Photosensitivity and radiation flux for three sources

Flux for tungsten lamps relative to λ3184 as unity; mercury arc relative to λ3130 as unity. Data of Pflüger (Kayser's Handbuch) are chosen since they give the same ratio of intensities at 3130 and 2537 as our thermopile readings.

Source	Wave-length	Relative flux $J_\lambda \Delta\lambda$	Sensitivity for equal flux 182°C	230°C
Mazda lamp	3880A	28.0	....	.006
	3610	12.4	.038	.051
	3480	7.9	.069	.092
	3400	5.4	.092	.129
	3350	4.0	.156	.216
	3310	3.1	.20	.27
Quartz-tungsten lamp	3300	1.64	.18	.28
	3280	1.47	.25	.33
	3260	1.35	.37	.41
	3240	1.25	.54	.54
	3220	1.15	.76	.72
	3200	1.05	.93	.90
	3180	.95	1.00	.97
	3160	.85	.92	1.00
	3140	.79	.84	.97
	3120	.73	.73	.86
	3100	.67	.69	.75
	3060	.57	.52	.60
	3020	.47	.40	.48
	2980	.38	.33	.40
	2940	.32	.28	.33
	2900	.26	.19	.27
	2860	.21	.15	.21
	2820	.16	.14	.18
	2780	.13	.12	.17
Mercury arc		Thermopile		Pflgüer
	3130	1.0	.78	1.0
	3030	.27	.34	
	2970		(.35)	.3
	2650		.2	.2
	2537	.67	.42	.6

The measurements for wave-lengths greater than λ3300 may be shown to advantage on a much larger scale (Fig. 2). This figure includes data for 162° and 230°C and in the upper portion of the drawing a map of the principal series lines. The peaks coincide with the series lines within the precision of the monochromator setting; apparently the widths are

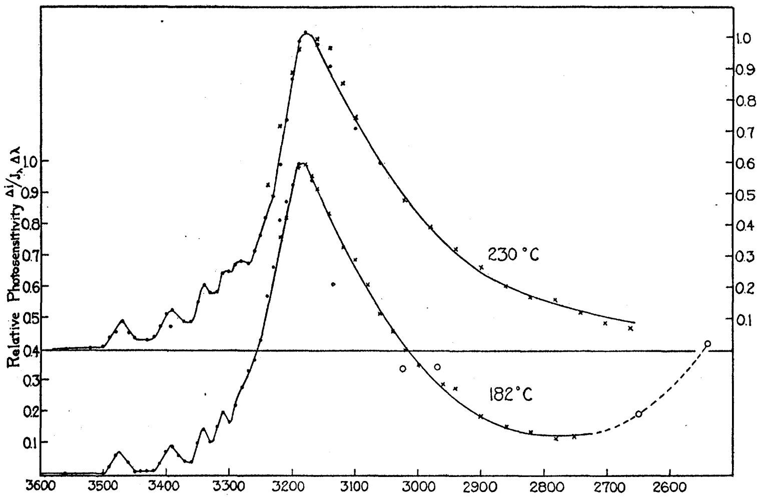

Fig. 1. Relative photosensitivity of caesium vapor corrected for an equal energy spectrum. The maximum sensitivity occurs at the limit 1*s* of the principal series.

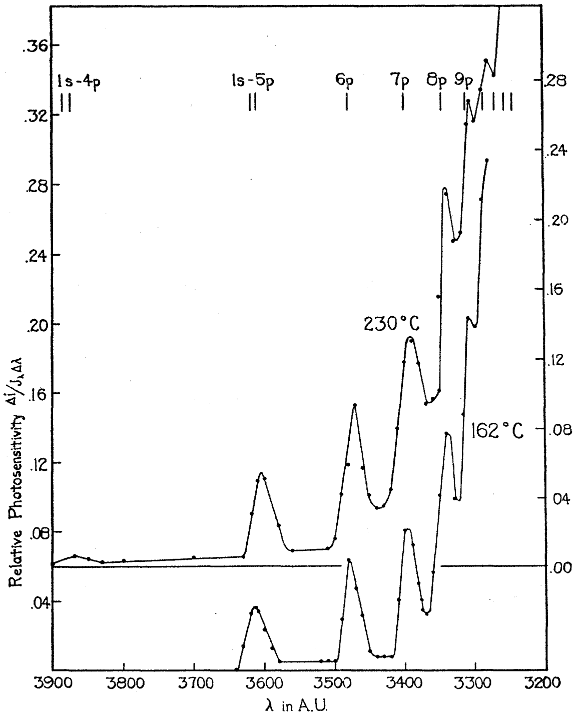

Fig. 2. Relative photosensitivity of caesium vapor on the long wave-length side of the photo-electric threshold. The peaks coinciding with the principal series lines are due to the ionization of excited atoms by interatomic collision.

determined by the resolving power of the instrument. Thus the observed effect for wave-lengths longer than λ3300 is largely if not entirely due to the separate lines. One may safely assume that in the range λ3300 to 3184 the curves show the unresolved effects of the closely-spaced higher members of the principal series.

INTERPRETATION OF EXPERIMENTAL DATA

Direct photo-electric ionization. Let us consider the numerical relationship involved between the observed photo-electric current and certain atomic properties of the vapor. If I_ν is the intensity of isotropic radiation of frequency ν, we may define the quantity B_ν such that $B_\nu I_\nu d\nu dt$ is the probability that an atom in the normal state absorbs a quantum of radiation and becomes ionized in the time dt under the influence of this radiation.[3] Let a beam of radiation having the solid angle $d\omega$ be incident at the angle ϑ on an element dS of the vapor surface. The amount of energy falling upon dS in the time dt is therefore $I_\nu d\nu \cos\vartheta dS\, d\omega\, dt$. If k_ν is the mass absorption coefficient and ρ is the vapor density, the fractional amount of energy absorbed by the thickness dx is $k_\nu \rho dx/\cos\vartheta$. Hence

$$\text{Energy absorbed in time } dt = I_\nu d\nu\, dS\, d\omega\, dt\, k_\nu \rho dx \tag{1}$$

This energy is also given by the product of (the number of atoms in the volume under consideration) × (the probability of absorption by a single atom) × (the correction for lack of isotropism of the beam) × (the energy of a quantum) as follows.

$$\text{Energy absorbed in time } dt = N\, dS\, dx \cdot B_\nu I_\nu d\nu dt \cdot (d\omega/4\pi) \cdot h\nu \tag{2}$$

where N is the number of atoms per cm^3. On equating (1) and (2) we find

$$k_\nu \rho / h\nu = B_\nu N/4\pi \tag{3}$$

Eq. (3) therefore gives a simple relation between the mass absorption coefficient and the Einstein probability factor B_ν.

Let $E_\nu = J_\nu d\nu = J_\lambda d\lambda =$ the energy flux between ν and $\nu + d\nu$ in ergs per sec. per cm^2 surface of the vapor taken normal to the beam. Then at the depth x the flux is given by

$$E_\nu' = E_\nu e^{-k_\nu \rho x}. \tag{4}$$

For the small values of $k_\nu \rho x$ concerned in the present work, on putting the energy absorbed $(E_\nu - E_\nu')$ equal to ΔE_ν this reduces to

$$\Delta E_\nu = E_\nu k_\nu \rho x. \tag{5}$$

The number of quanta absorbed is $\Delta E_\nu / h\nu$ and if the absorption of each quantum results in the production of an ion, this is equal to the number

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[3] See Milne, Phil. Mag. **47**, 209 (1924).

of ions produced per second per cm^2 of cross-sectional beam area and depth x. The total number of ions n, produced in the ionization chamber of volume $w(=x\times$cross section of beam) is therefore

$$n=E_\nu k_\nu \rho w/h\nu \tag{6}$$

Let $i=$number of electrons emitted by the hot wire per second when the current is limited by space charge, and $\Delta i=$increase in this number due to the presence of ions, then

$$\Delta i=Rn \tag{7}$$

where R by definition represents the number of electrons which a single ion is capable of releasing by partial neutralization of the negative space charge. The characteristics of this quantity will be considered below. On substituting the value of n from Eq. (6) and by use of Eq. (3) we finally obtain

$$\Delta i=(RE_\nu wN/4\pi)B_\nu. \tag{8}$$

The increase in current Δi, on illumination, is given by the galvanometer deflection. Theoretically E_ν could be evaluated absolutely by use of the spectrothermopile although with the sensitivity at our disposal the best that could be hoped for was a rough estimate of the energy over a very wide spectral range. Thus if R were known, an approximate estimate of B_ν in absolute value could be obtained. While this is a very indirect method of evaluating B_ν it would appear to offer greater possibilities than the direct determination of the absorption coefficient and the use of Eq. (3). For example Harrison's data[4] on sodium under dynamic equilibrium, as nearly as may be estimated from the tabulated measurements, indicate a mass absorption coefficient, on the short wave-length side near the limit, of $k_\nu=3\times10^{-4}$ or an atomic coefficient $=k_\nu\rho/N=10^{-18}$. Since Harrison and Slater present evidence that with the rapidly distilling vapor at the high temperatures employed there are about 50 times as many diatomic molecules as atoms, the consideration of this coefficient as an atomic constant is, of course, questionable; however, it may indicate order of magnitude. The physical process occurring in photoelectric absorption near the limit is the same for all alkalies so that caesium should have an atomic absorption coefficient of the same order of magnitude as sodium. At the highest pressure we employed, 500 bars, an absorption coefficient of 10^{-18} would necessitate a tube 900 cm in length for an absorption of 50 percent. The experiment, therefore, is not promising for observations under static equilibrium, whereas, by the photo-

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[4] Harrison, Phys. Rev. **24,** 474 (1924); Harrison and Slater, idem **26,** 176 (1925).

electric method described, operation at much lower pressure, with a resulting increase in the relative concentration of monatomic vapor, is quite satisfactory.

We have attempted to evaluate R the efficiency factor of the tube. Measurement of the current produced by illumination when the filament is not heated should give the ion current plus the photo-electric emission from the filament, the latter being slightly negative to the cylinder. It was hoped that from measurements at different pressures, the second factor could be eliminated, but the results were not sufficiently reproducible. The data indicate that R is greater than 10^4 at the highest pressure employed and may be as large as 10^6 at lower pressures.

Kingdon[5] used a tube especially designed for the determination of R and in certain cases observed values as great as 300 times the mobility ratio of ions to electrons at low pressure, corresponding to 10^5 for caesium. He also found that R was proportional to the $-2/3$ power of the pressure. Using data in Table I of our earlier paper, one finds that Δi is proportional to $p^{0.4}$, and remembering that N in Eq. (8) is proportional to p, this gives R as proportional to $p^{-0.6}$, in fair agreement with Kingdon. The factor R besides depending upon the general geometry of the apparatus involves the recombinations which occur between the ions and electrons. With the weak fields employed for our work, it is very sensitive to changes in applied potential or space charge as altered by varying the filament temperature. The space charge may be appreciably affected by intense illumination and the resulting production of ions, especially at the higher pressures. If however, the value of Δi is not greater than possibly 1 percent of the total thermionic current i, the direct proportionality between Δi and E_ν as a variable is quite accurately fulfilled; that is, R remains a constant. This relation was carefully checked by use of wire gauze absorption screens and all of the observations recorded in the present paper are within the prescribed limit. One must finally consider whether or not R depends upon the frequency ν. The tube is sensitive to the production of ions and insensitive to electrons. All the ions are of the same type regardless of the radiation by which they are produced. The photo-electrons to be sure are ejected with a velocity dependent upon ν, but especially when present to only 1 part in 10^7, in order of magnitude, of the normal thermionic current i it seems impossible that R may be affected by small changes in ν.

Hence, according to Eq. (8), for Δi small compared to i and with constant experimental conditions, i.e., vapor pressure, temperature, filament

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[5] Kingdon, Phys. Rev. **21**, 408-18 (1923); our R is equivalent to Kingdon's α.

temperature and applied potential, Δi is directly proportional to $E_\nu B_\nu$. Since $E_\nu = J_\nu d\nu = J_\lambda d\lambda$ or, considering the finite slit width, since $E_\nu = J_\lambda \Delta\lambda$ we have

$$\Delta i = KJ_\lambda \Delta\lambda B_\nu \tag{9}$$

where K is a proportionality constant. The curves of Figs. 1 and 2 and the data in Table II represent relative values of $\Delta i/J_\lambda\Delta\lambda$ as a function of λ. Hence, the ordinates of the curves give the relative values of the probability coefficient B_ν for a ν value corresponding to the indicated λ. We believe that with especially designed apparatus the absolute values of B_ν may be obtained with some accuracy as indicated above, but for the present only relative values will be considered.

Since B_ν is an atomic constant, it should be independent of the pressure. This is qualitatively confirmed by the geometrical similarity of the two curves of Fig. 1 and several other curves not here reproduced. There are no data available in the literature for direct comparison. The lower curve shows an apparent increase in photosensitivity between λ2700 and 2500. The evidence is based chiefly on the measurements with the mercury line λ2537. Lawrence has suggested to us that this increase may arise from ionization of caesium molecules, an explanation consistent with his results for potassium vapor.[6] Another possibility is that merely a trace of mercury was present with the cycle of phenomena: absorption of λ2537; excited mercury atom; collision of the second type; highly excited caesium atom; completion of ionization by collision. While the usual precautions were taken to exclude mercury by baking the apparatus, etc., a small amount in the caesium could not have been completely removed by distillation. Spectroscopic examination of the vapor in a discharge at 10 volts failed to show any mercury lines, but prominent lines of rubidium and potassium were observed. These impurities could not have been present in a concentration sufficient to have affected our data. The caesium chloride from which the caesium was prepared by distillation in the presence of calcium was supposed to be fairly pure. Several fractional distillations in vacuum were made at low temperature which should have increased the purity since both potassium and rubidium have one fifth the vapor pressure of caesium at 250°C. Finally the percentage impurity present in the metal is reduced in the vapor by at least the factor 5 on account of the vapor pressure ratio. No evidence for either of these impurities was detected in the photosensitivity curves which, with an appreciable impurity, should have shown increased sensitivity at the corresponding principal series limits.

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[6] Lawrence, Phil. Mag. **50,** 345 (1925).

In the x-ray range B_ν is fairly well known empirically as a function of ν or of λ. Referred to a particular x-ray level it is a discontinuous function equal to zero for wave-lengths greater than the absorption limit and is approximately proportional to λ^4 for shorter wave-lengths. Various attempts have been made to derive theoretically the form of the B_ν curve, notably by Kramers,[7] Milne[8] and Becker.[9] For an isotropic radiation field they find the relation between the probability of absorption of a quantum $h\nu$, resulting in ionization, and the chance of recombination of an ion with an electron of velocity v where ν and v are related by the photo-electric equation

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_1 \tag{10}$$

ν_1 being the limit of the absorption series. The chance of recombination may be expressed in terms of the "effective collision area" q for an encounter resulting in recombination. The general relation between B_ν and q is

$$B_\nu/q = (\nu-\nu_1)/\nu^3 \times \text{constant}. \tag{11}$$

By the introduction of rather speculative assumptions as to the law of recombination, the following results are obtained. Kramers finds B_ν proportional to ν^{-4} or to λ^4. Milne's work leads to a proportionality between B_ν and ν^{-3} or λ^3 in which he excludes its applicability to x-rays, although the argument for this is by no means apparent.[10] Becker derives the relation

$$B_\nu = \frac{1}{(\nu-\nu_1)\nu^3}\left[1 - \frac{(\nu-\nu_1)^2}{4\nu_1^2}\right] \times \text{constant}. \tag{12}$$

Eq. (12) is not applicable near the limit since it becomes infinite for $\nu = \nu_1$. Fig. 3 shows the form of these three theoretical relations, expressed by B_ν as a function of λ, together with our experimental values. The λ^3 and the λ^4 laws entirely fail in representing the data but satisfactory agreement with Becker's equation obtains in the range $\lambda 3050-2700$. An empirical relation of the form $B_\nu = B_{\nu_1} e^{-a(\lambda_1-\lambda)}$ where $\lambda_1 = 3184$, and B_{ν_1} is the value of B_ν at this wave-length, represents the observations in the range $\lambda 3184-2600$. If the data by Harrison on the absorption of the mixture of sodium atoms and molecules at high pressure are converted into relative B_ν values by use of Eq. (3) the general shape of curve ob-

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[7] Kramers, Phil. Mag. **46**, 836-71 (1923).

[8] Milne, Phil. Mag. **47**, 209-41 (1924).

[9] Becker, Zeits. f. Phys. **18**, 325-43 (1923).

[10] Milne loc cit. p. 229.

tained resembles our measurements, certainly in preference to a third or fourth power relation.

For the spectral range λ3050 to 2700 the second term in brackets in Eq. (12) is negligible. Hence on combining this expression with Eq. (11) one finds

$$q=\frac{\nu^3}{\nu-\nu_1}B_\nu \times \text{const.} = \frac{\text{const.}}{(\nu-\nu_1)^2}$$

and by Eq. (10)

$$q=\text{const.}/v^4=\text{const.}/V^2 \tag{13}$$

where V represents the velocity of an electron expressed in volts. This law is consistent with our observations between 0.15 and 0.5 volt. For lower voltages there is a wide departure. Eq. (13) is the Thomson law of recombination and cannot apply at low speeds since q must satisfy the condition that in Eq. (11) B_ν is finite when $\nu=\nu_1$.

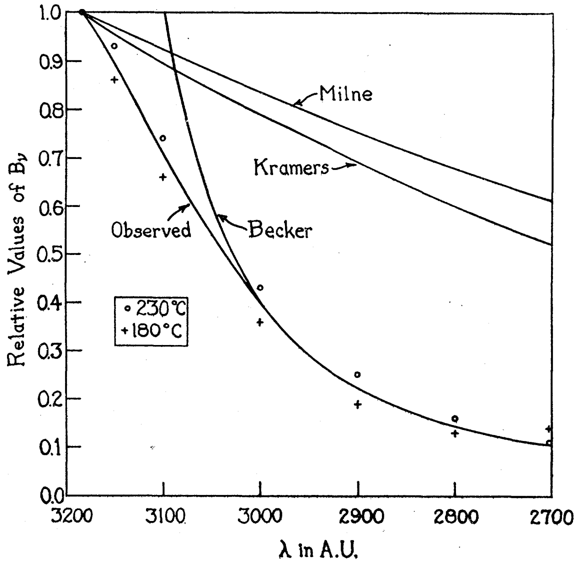

Fig. 3. Observed absorption probability of the caesium atom as a function of λ and graphs of the theoretical relations derived by Milne, Kramers and Becker.

Photo-ionization by line absorption. The observed relative sensitivity for direct photo-electric ionization, on the short wave-length side of the limit, and indirect ionization at points corresponding to the principal series lines depends upon the resolution of the monochromator. If both entrance and exit openings are doubled, the width of spectrum transmitted and the energy flux at each point in the exit slit are approximately doubled. When the vapor absorbs a continuous band the energy available for photo-electric ionization is therefore multiplied by four. At $\lambda 3200$, the principal series lines are so close together that roughly the absorption may be considered as continuous so that even here the four-fold change in sensitivity should be expected, as illustrated by the data in Table I. If the absorption line is narrow compared to the slit width and lies in the spectral region corresponding to the first few terms of the principal series where the monochromator may differentiate definitely between the effects due to the adjacent members, doubling both slits approximately doubles the sensitivity of the tube. That is, the increase in heterochromatism of the beam produces no effect since the absorption is selective. At the low pressures employed, the absorption lines are very narrow so by decreasing the slit width the ordinates on the long wave-length side of a photosensitivity curve, such as Fig. 1, may be increased relative to those on the short wave-length side. Theoretically this process could be continued until the slits and absorption lines were of comparable width. The significance of the curve in the transitional region between these two conditions is therefore quite indefinite.

Table III shows the relative sensitivity of the tube at wave-lengths corresponding to the six principal series lines $1s-4p$ to $1s-9p$, a spectral region, except possibly for the last line, which is outside of the transition stage mentioned above. The small corrections for dispersion of the monochromator have been removed from these values since the lines are narrow compared with the slit width. The numbers represent the relative heights of the observed peaks measured from the axis of zero sensitivity thus neglecting the small effect due to scattered radiation. While the lines are somewhat superposed, the sensitivity contributed by one line to the *observed peak* of a neighboring line does not become appreciable for wave-lengths greater than $1s-9p$. Some change in relative sensitivity at the peaks for different temperatures is indicated but for the

TABLE III

Photo-ionization by line absorption
(Relative sensitivity at absorption lines)

Temp.	$1s-4p$ (3880)	$1s-5p$ (3611)	$1s-6p$ (3480)	$1s-7p$ (3400)	$1s-8p$ (3350)	$1s-9p$ (3314)
230°C	.1	.62	1.0	1.30	2.08	2.5
203	.12	.64	1.0	1.38	1.90	2.5
182		.62	1.0	1.24	2.00	2.5
161		.66	1.0	1.23	2.00	2.8
149		.70	1.0	1.36	1.98	3.3
134		.60	1.0	1.43	1.67	2.6
128		.60	1.0	1.15	1.32	1.9

pressure range represented, 5 to 500 bars, it is surprising to find the data so nearly constant.

The observed photo-ionization arises from a type of multiple excitation. From the data presented in the first paper, it was concluded that atoms in an excited state having a low ionization potential as a result of line absorption, may be ionized by collision with other atoms. The values given in Table III permit an extension of this idea. The probability of ionization depends upon at least three factors: (1) probability of absorption, (2) chance that the kinetic energy of collision is sufficient to complete ionization and (3) chance that the excited state persists or is passed on by resonance until collision occurs.

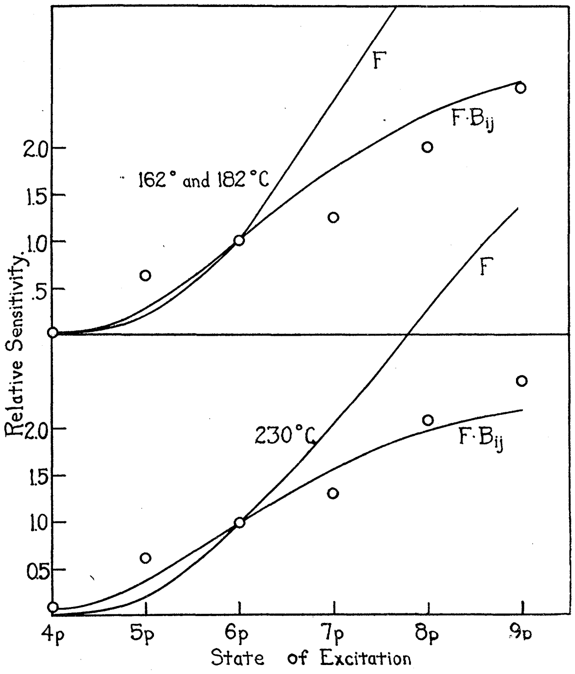

Fig. 4. Observed photosensitivity, represented by circles, of the caesium atom on the long wave-length side of the 1*s* limit. The curve FB_{ij}, except for a small variable and unknown factor, is the probability for the occurrence of the physical process responsible for the sensitivity.

The first factor depends upon the probability B_{ij} that the atom in the normal state i absorbs a quantum and passes over to the state j. These probability factors are unknown for the caesium lines here concerned but Ladenburg[11] has shown that the principal series of the alkalies are much

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[11] Ladenburg, Zeits. f. Phys. **4**, 451-68 (1921).

alike in this respect so we may use the data by Harrison[12] for the relative probabilities in sodium. The chance of ionization by collision from an excited *mp* state may be estimated roughly by use of the kinetic gas theory. In the earlier paper this factor was designated by F. The third probability is unknown but is nearly unity at higher pressures. Fig. 4 shows the relative, observed photosensitivity at the successive lines, plotted as circles, and relative values of F and FB_{ij} for two temperature ranges. Qualitatively the agreement is excellent.

It is of interest that these experiments on the long wave-length side of the photo-electric limit yield a map of the principal series somewhat similar to an emission spectrum, yet no emission is taking place; in fact the sensitivity depends upon the suppression of the emission.

The authors desire to thank Dr. Sebastian Karrer of the Fixed Nitrogen Laboratory for lending them the quartz monochromator.

BUREAU OF STANDARDS,
WASHINGTON, D. C.
October 5, 1925.

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[12] Harrison, Phys. Rev. **25**, 768-82 (1925).