

THE PHOTO-IONIZATION OF THE VAPORS OF CAESIUM AND RUBIDIUM

BY ERNEST O. LAWRENCE AND N. E. EDLEFSEN
UNIVERSITY OF CALIFORNIA AT BERKELEY

(Received June 6, 1929)

ABSTRACT

A modification of Foote and Mohler's space charge method for the measurement of photo-ionization was devised which compensated out spurious effects due to fluctuations of temperature and increased the useful sensitivity of the space charge to positive ions about one hundred fold. By measuring simultaneously photo-ionization and light intensities the following results have been obtained. In caesium, the ionization per unit light intensity B_ν varies with frequency ν (over the range 2200A to 3130A) according to the equation

$$B_\nu = \frac{\text{const}}{\nu^3(\nu - \nu_0)}$$

This relation also represents fairly well the experimental observations of B_ν in rubidium. Thus, the continuous absorption resulting in ionization decreases with wave-length much more rapidly than the analagous absorption beyond the Lyman and Balmer series limits as calculated on the wave mechanics by Sugiura, Oppenheimer, and Reiche. The results, moreover, are not even qualitatively similar to Hargreaves' calculation of the variation with frequency of B_ν for lithium. Assuming the principle of detailed balance it follows from these experiments that the effective collision capture cross-sections of caesium and rubidium ions for electrons vary inversely as the square of the energy of the electrons relative to the ions. This is the Thomson recombination law and has been derived on the wave mechanics by Oppenheimer for the recombination of protons and electrons. The existence of photo-ionization by absorption of principal series lines in caesium, so clearly exhibited by Mohler, Foote and Chenault, has been confirmed and also has been observed in rubidium.

EXPERIMENTAL difficulties have hampered studies of photo-ionization of the alkali vapors and results obtained have been somewhat meagre and apparently inconsistent. For example, Samuel¹ observed appreciable ionization of potassium vapor only by wave-lengths near the head of the principal series while on the other hand Williamson² and Lawrence³ have concluded from their experiments that the probability of ionization increases rapidly as one passes to shorter wave-lengths. Further, in caesium vapor Kunz and Williams⁴ found ionization setting in exactly at the series limit while Foote and Mohler⁵ have obtained convincing evidence that caesium is ionized by wave-lengths considerably longer, the ionization efficiency being only a maximum at the series limit. There are several rather cogent argu-

¹ Samuel, Zeits. f. Physik **29**, 209 (1924).

² Williamson, Proc. Nat. Acad. Sci. **14**, 793 (1928).

³ Lawrence, Phil. Mag. **50**, 345 (1925).

⁴ Kunz and Williams, Phys. Rev. **22**, 456 (1923).

⁵ Foote and Mohler, Phys. Rev. **26**, 195 (1925).

ments leading to the conclusion that the ionization probability should indeed have a maximum value at the limit and moreover should decrease monotonically on passing to shorter wave-lengths. Mohler, Foote and Chenault⁶ do not confirm the latter inference, however, for they find that the ionization probability has a minimum value in the region of 2700Å and rises rapidly with decreasing wave-lengths attaining a magnitude of 40 percent of the series limit value in the region of 2536Å. Little⁷ has confirmed qualitatively their observations. It has been suggested that the ionization by wave-lengths on the long wave-length side of the minimum may be of caesium atoms only while the setting in of molecular ionization by shorter wave-lengths may be responsible for the subsequent rise of the ionization probability curve. It appears on this view that molecular ionization should predominate in potassium vapor since relatively many more molecules are always present and therefore the probability of ionization should be observed as a quantity which increases to shorter wave-lengths from a threshold value itself of wave-length shorter than the series limit—very much as observed by Lawrence.

The lack of agreement of the experimental observations of the various investigators however does not permit one to deduce with confidence the experimental laws governing the several photo-ionization processes. It is of importance to establish these laws because the alkalis are hydrogen-like and are readily susceptible to theoretical treatment. Contributions to this end are contained in the present paper and in another to follow on the photo-ionization of potassium vapor.

THE EXPERIMENTAL METHOD

The experimental difficulties involved in studies of the photo-ionization of the alkalis were largely overcome by Foote and Mohler's⁵ ingenious application of Kingdon's⁸ observations of the neutralization of space charge around a filament by spiralling positive ions. Their method possesses great inherent sensitivity, for one ion in the course of time effectively neutralizes the space charge of as many as a million electrons. In order to achieve the greatest sensitivity possible using Foote and Mohler's method, which involves balancing out the thermionic emission by a potentiometer arrangement, it is clearly necessary to maintain the total electron emission constant to better than one part in a million—admittedly a difficult experimental feat. We have modified their arrangement so as to compensate out fluctuations of the thermionic emission due to changes in temperature of the filament and thereby have increased the useful sensitivity of the space charge method probably one hundred fold.

Figure 1 shows diagrammatically the arrangement. A 5 mil tungsten filament extended concentrically through two cylinders P_1 , P_2 15 mm in diameter and 25 mm in length. Adjacent ends of the cylinders were closed

⁶ Mohler, Foote and Chenault, *Phys. Rev.* **27**, 30 (1927).

⁷ Little, *Phys. Rev.* **30**, 109 (1927).

⁸ Kingdon, *Phys. Rev.* **21**, 408 (1923).

excepting for 2 mm holes while the other ends were open. P_1 and P_2 were attached to adjustable resistances R_1 and R_2 of about 10,000 ohms. A sensitive galvanometer G was connected across the cylinders and resistances as the diagram indicates. The cylinders were approximately symmetrical relative to the filament and therefore received nearly equal portions of the electron emission. A battery maintained them about one volt positive to the filament so that the thermionic current was limited by space charge. The heating current through the filament and the potential difference between filament and cylinders were adjusted to give the maximum sensitivity to positive ions. Usually under such conditions the thermionic current was about $5(10^{-5})$ amps. The resistances R_1 and R_2 were adjusted so as to have across them equal differences of potential arising from the thermionic current, a condition indicated by a null deflection of the galvanometer. Under these circumstances fluctuations in the electron emission due to changes of

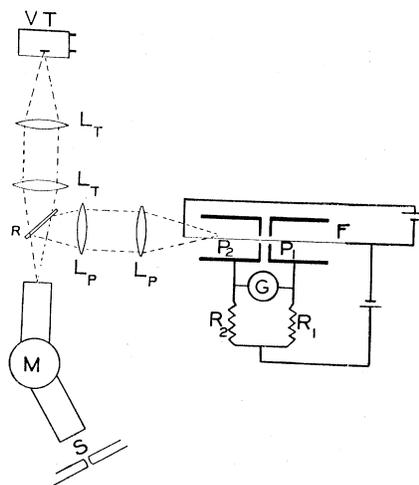


Fig. 1.

temperature of the filament produced approximately equal changes in the voltage drops across the resistances, causing thereby no sensible deflection of the galvanometer. The galvanometer responded only when the percentage changes of the currents through the resistances were not equal. This occurred when the region of P_2 was irradiated by light forming ions in the vapor which were drawn towards the filament and, spiralling around, increased the space charge limited electron emission to P_2 . For small current changes due to neutralization of space charge by the ions, the galvanometer deflections were proportional to the rate of ionization of the vapor.

This compensation scheme was so effective that with quite ordinary precautions to keep conditions constant the galvanometer zero remained within the same millimeter scale reading for considerable periods of time. In most of the work a deflection of 0.2 mm of a galvanometer having a sensitivity of $2(10^{-10})$ amps per mm could be detected with certainty.

Thus, since the total thermionic emission was usually about $5 (10)^{-5}$ amps, it was possible to detect changes in the thermionic emission due to photo-ionization of the vapor of about 1 part in 10^6 .

This arrangement eliminated any remaining difficulty in measuring photo-ionization in the alkalis—even in potassium vapor—and reduced the problem of accurately determining the law of variation of ionization with frequency in caesium to finding a steady source of continuous ultra-violet light which after resolution into narrow bands of wave-lengths would be sufficiently intense to be measured by a thermopile. To this end a water-cooled hydrogen discharge tube able to carry 5 amps at 3000 volts was developed.* The tube had a diameter of 7 mm and, as far as we know, produced current densities about 10 times greater than anyone has used before in a similar type of discharge. The discharge proved to be a highly steady source of ultra-violet light, giving bands from twenty to forty angstroms wide of sufficient intensity to be measured by a vacuum thermopile in conjunction with photoelectric amplification of the galvanometer deflections and was used for the experimental study of caesium. An iron arc was used in the observations of photo-ionization of rubidium.

Light from the source *S*, resolved by a Bausch and Lomb monochromator *M* into wave-length bands (slits 0.2 mm) passed to a quartz plate *R* where a portion was reflected and another portion passed through. The transmitted portion was collimated and focused on a vacuum thermopile *VT* by the lenses *L₁*. Similar lenses focused the reflected portion in the cylinder *P₂* of the photo-ionization tube. An additional quartz plate was inserted in the optical path to the photo-ionization tube which made the two optical paths (from *R* to *VT* and *P₂*) through quartz as well as air very nearly equal. Frequent tests insured that the lenses focused all of the light on the thermopile and in the region of *P₂*. Clearly this optical arrangement allowed simultaneous measurement of photo-ionization and light intensities, leading to values for the relative ionization per unit light intensity free from serious systematic errors.

It was found in preliminary experiments that the presence of a trace of mercury vapor gave rise to very large photo-ionization by light of wave-length 2536A, being evidently due to absorption of the light by the mercury atoms and collisions of the second kind. To eliminate such spurious effects care was taken to reduce to a minimum the presence in the tube of gases and vapors other than the alkali under investigation. The tube was of Pyrex with a quartz window joined to it by a graded seal. It was carefully baked out at 500°C and the metal parts were glowed till all traces of gases were removed. Caesium—or rubidium—introduced into a side tube by heating calcium filings with its chloride, was successively distilled into a series of constricted tubes which had received the baking at 500°C and finally into the photo-ionization tube which then was sealed off from the side tubes and the pump.

* A description of this ultra-violet source will be submitted for publication elsewhere.

RESULTS

Caesium. Figure 2 exhibits the dependence of the relative probability of ionization of caesium vapor on wave-length. The ordinates record the ionization per unit light intensity produced by wave-length bands (20 to 40A) from the monochromator set at wave-lengths given by the abscissas. The ordinates are in arbitrary units because the nature of the method of observation of the photo-ionization does not allow direct determination of absolute values. The circles and dots represent two sets of data taken by

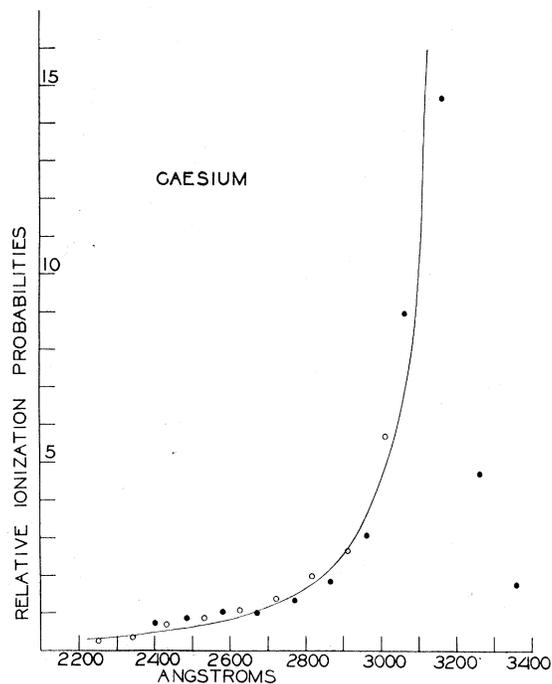


Fig. 2. The wave-length dependence of the ionization per unit light intensity B_ν in Cs. The circles and dots record two sets of observations while the curve represents $B_\nu = \text{const.}/\nu^3(\nu - \nu_0)$.

different observers during the same evening with the photo-ionization tube at a temperature of 180°C. These data indicate that the probability of ionization B_ν decreases rapidly with wave-length from the series limit along the curve of Fig. 2 which is a plot of the relation

$$B_\nu = \frac{\text{const}}{\nu^3(\nu - \nu_0)}$$

ν_0 being the series limit frequency. There is apparently a very slight deviation of the data from the curve in the region of 2500 to 2700A and in the preliminary experiments the deviation was more pronounced, some of the results showing an actual rise in the probability of ionization having a

maximum near 2500Å. However, at no time was there observed a probability of ionization at 2500Å which was greater than 1/8 of the series limit value. It now seems probable that the earlier observations were due to the presence of impurities in the caesium vapor. There remains, however, always the possibility that the quartz window of the photo-ionization tube possessed throughout the experiments an invisible film which absorbed ultra-violet light, introducing thereby a systematic error. We regard this possibility as highly improbable.

The study of caesium was concentrated on the region of wave-lengths well beyond the series limit where the observations of Mohler, Foote and Chenault and Little indicated a minimum in the ionization probability curve. However, several runs throughout the spectral range were made confirming the existence of ionization by wave-lengths longer than the series limit which Mohler, Foote and Chenault exhibited so well. The results presented here differ from the previous observations—in addition to showing no minimum in the probability of ionization curve—in that the decrease of the ionization probability B , beyond the limit is definitely more rapid. This discrepancy between the present work and the observations of Mohler, Foote, and Chenault is not surprising when it is recalled that in their work the light intensities were not measured simultaneously with the observation of ionization but were estimated from knowledge of the spectral energy distribution in the source and the probable transmission characteristics of the optical system. We cannot reconcile satisfactorily, however, Little's results with the present data.

Though the space charge method does not allow measurement of absolute values of ionization it may be useful to record the general order of magnitude of the various quantities involved in the experiments. A current of three amps passing through the hydrogen discharge tube gave a continuous spectrum of ultra-violet light of such intensity that when resolved by the monochromator into bands of 20Å in the region of 2200Å produced a deflection of the thermopile galvanometer of 0.1 mm. These rather small deflections were readily amplified one hundred fold by a photoelectric cell arrangement similar in principle to thermo-relay devices now widely used. These wave-length bands produced deflections of the photo-ionization galvanometer of about 1 cm corresponding to a change in the thermionic current of $2 (10^{-9})$ amp. In the region of 2500Å the thermopile galvanometer deflections were about 3 times as great.

Rubidium. Two independent sets of observations of the ionization of rubidium are shown in Fig. 3. The crosses represent data taken at a temperature of 197°C while the circles record observations taken with the photo-ionization tube at a temperature of 245°C. The good general concordance of the two sets of observations attests to the trustworthiness of the results and show rather definitely that the ionization probability function is independent of the vapor pressure and temperature over this range. An iron arc source was here used which because of its unsteadiness gave rise to the rather large, as compared to the caesium observations, fluctuations of

the experimental observations. The dependence on wave-length of the ionization probability B_ν in rubidium clearly is very much the same as in caesium. On the long wave side of the series limit ionization by line absorption is evident, merging into the continuous absorption at the limit where B_ν is a maximum. The successive peaks in the probability curve correspond to lines of the principal series (indicated in the Fig. along the abscissa axis) excepting the peak at 3490A which is of unknown origin. Though the plot of the experimental data suggests that ionization by absorption of light of frequency of one of the principal series lines near the limit is less probable

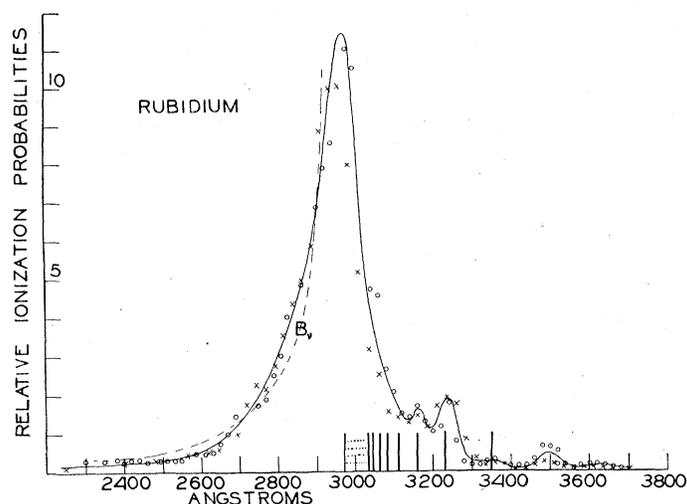


Fig. 3. The ionization in Rb per unit light intensity B_ν . The circles and crosses record observations at temperatures of 197°C and 245°C respectively. The broken curve represents the equation $B_\nu = \text{const.}/\nu^3(\nu - \nu_0)$. The principal series lines converging to the limit are represented along the abscissas.

than ionization by light of slightly greater frequency than the series limit, it is to be borne in mind that the converse is probably true. The reason for this is evident when it is realized that on the long wave-length side of the series limit the ionization is produced by only a very small part of the band of wave-lengths whose total intensity is measured. Beyond the limit the ionization probability decreases with wave-length possibly slightly less rapidly compared to the corresponding variation in caesium. The dotted curve B_ν represents again

$$B_\nu = \frac{\text{const}}{\nu^3(\nu - \nu_0)}$$

where ν_0 is the series limit frequency. The experimental observations of B_ν show a slight deviation from this curve. The data are hardly accurate enough, however, to warrant concluding definitely that this deviation is real.

DISCUSSION

Until recently formulae expressing the variation with wave-length of absorption coefficients were derived by statistical reasoning from the principle of detailed balance. Sugiura,⁹ Oppenheimer,¹⁰ and Reiche¹¹ have now obtained independently from the quite different standpoint of the wave mechanics expressions for the dependence on wave-length of the continuous absorption beyond the Lyman and Balmer series limits in hydrogen. They agree in finding that the continuous absorption decreases with wave-length but are not in precise accord as to the rate of decrease. Sugiura and Reiche find beyond the Lyman limit a λ^5 law obtaining while Oppenheimer finds a $\lambda^{4.3}$ decrease. The alkalis are hydrogen-like and therefore it appears that their regions of continuous absorption should resemble the continuous absorption of hydrogen atoms in various stages of excitation. Thus for example the absorption by lithium should take a course similar to the absorption beyond the head of the Balmer series and caesium atoms should have absorption characteristics like those of hydrogen atoms in the 6*S* level. Now the ionization probability in caesium decreases with wave-length much more rapidly than the fourth or fifth power of the wave-length, being more closely represented by a twelfth power law. It is interesting to observe, however, that Sugiura finds for the absorption beyond the Balmer limit a more rapid decrease with wave-length (λ^6) compared to the Lyman continuous absorption (λ^5) suggesting that the wave mechanics would predict for the continuous absorption by hydrogen in the 6*S* level a much more rapid decrease resembling more closely the caesium absorption.

Hargreaves¹² has carried through a calculation of lithium absorption probabilities using Hartree's approximation method of self-consistent fields and obtains a quite surprising result, for he finds that continuous absorption increases to a maximum value at a very considerable distance beyond the head of the series (about 1.3 equivalent volts) where a continuous decrease sets in which is somewhat less rapid than a λ^4 law. The present experimental results, which one has every reason to believe should be qualitatively similar to the absorption law for lithium, are clearly not in agreement with Hargreaves' predictions.

Returning to the older theories of transition probabilities based on the principle of detailed balance it may be recalled that such theories yield directly the variation with frequency of the ratio B_ν/q_ν , namely,

$$B_\nu/q_\nu = \text{const } (\nu - \nu_0)/\nu^3 \quad (1)$$

where B_ν is the probability that an atom will be ionized by light of unit intensity and frequency ν in unit time and q_ν is the effective collision capture cross-section of the corresponding ion for an electron moving with the velocity v relative to the ion specified by

⁹ Sugiura, *Jour. de Physique* **8**, series 6, 113 (1927).

¹⁰ Oppenheimer, *Zeits. f. Physik* **41**, 268 (1927).

¹¹ Reiche, *Zeits. f. Physik* **53**, 168 (1929).

¹² Hargreaves, *Proc. Camb. Phil. Soc.* **25**, 75 (1929).

$$\frac{1}{2}mv^2 = h\nu - h\nu_0$$

$h\nu_0$ being the ionization energy.

Various expressions for q_ν have been either postulated or given a more or less reasonable justification and have been used together with the above relation to evaluate the frequency dependence of B_ν . Milne¹³ assumed that the probability that an electron will be captured by an ion varies inversely as the square of its velocity relative to the ion and thereby got a λ^3 law for B_ν . Kramers¹⁴ obtained a λ^4 law. Becker¹⁵ derived the above relation between B_ν and q_ν and to illustrate the usefulness of the relation in getting B_ν he assumed that q_ν depends on electron velocity in the same manner that the probability that a canal ray will pick up an electron from a rest gas molecule depends on its velocity—as observed by Rückardt.¹⁶ Becker recognized that one could hardly expect such a probability law to be applicable to the recombination of ions and electrons and attached little importance to his expression for B_ν . Nevertheless, his expression is the right one for the photo-ionization of caesium up to within about fifty Angstroms of the series limit. The curve of Fig. 3 represents

$$B_\nu = \text{const}/\nu^3(\nu - \nu_0) \quad (2)$$

which is equivalent to Becker's expression, viz.

$$B_\nu = \frac{\text{const}}{(\nu - \nu_0)\nu^3} \left[1 - \frac{(\nu - \nu_0)^2}{4\nu_0^2} \right]$$

within the experimental error since the second term is negligible over the range involved.

If, instead of taking Rückardt's expression for q_ν , one assumes the Thomson recombination law, which is that recombination varies inversely as the square of the energy of the electron relative to the ion one obtains Eq. (2) which the present experimental data so accurately confirm. The experimental observations are quite free of serious systematic errors and the accuracy of the probability law established experimentally compares with the fluctuations of the experimental points about the smooth curve. Mohler, Foote and Chenault pointed out that their results were consistent with Becker's evaluation of B_ν and the Thomson recombination law as well over the spectral range 3050Å to 2700Å. The present results indicate that the laws are applicable over a much wider range 3100Å to 2200Å.

Thus, assuming the validity of the principle of detailed balance these experiments may be regarded as establishing, in addition to the variation of B_ν with frequency, that the effective collision capture cross-section of caesium and rubidium ions for electrons vary inversely as the square of the energy of the electrons relative to the ions. It is significant that Oppen-

¹³ Milne, *Phil. Mag.* **46**, 836 (1923).

¹⁴ Kramers, *Phil. Mag.* **46**, 836 (1923).

¹⁵ Becker, *Zeits. f. Physik* **18**, 325 (1923).

¹⁶ Rückardt, *Ann. d. Physik* **71**, 377 (1923); *Zeits. f. Physik* **15**, 164 (1923).

heimer¹⁷ using the wave mechanics has derived the same law for the recombination of protons and electrons, for it is rather to be expected that alkali ions and protons should exhibit such similar properties. There occurs the difficulty pointed out by Mohler and Boeckner,¹⁸ namely, that Oppenheimer's expressions for B_ν and q_ν do not fulfill the requirement of the principle of detailed balance as embodied in Eq. (1). The present results favor his evaluation of q_ν and therefore suggest that there may be an error in the derivation of B_ν . Such an inference is questionable, for indeed, the opposite would be deduced from the experiments of Mohler and Boeckner on the continuous spectrum of caesium vapor.

¹⁷ Oppenheimer, *Phys. Rev.* **31**, 349 (1928).

¹⁸ Mohler and Boeckner, *Bur. Stan. Jour. Res.* **2**, 489 (1929).