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RECOMBINATION AND PHOTO-IONIZATION.

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Contents

Introduction

EINSTEIN'S derivation of Planck's radiation law has introduced into physics a general method of deriving the numerical relation between the atomic constants involved in any two converse processes. Consequently experimental problems are facilitated inasmuch as there are two methods of approach available instead of one. The spontaneous recombination of an ion and an electron with emission of radiation and the converse process, ionization of an atom by absorption of radiation, are therefore two phases of the same problem.

A purely mechanical picture of the recombination process serves to visualize the atomic constants. If an electron approach a positive ion the path will be a hyperbola except as there is some dissipation of energy by radiation. The amount of radiation depends, according to classical theory, on the curvature of the path and speed which in turn depends on the distance between the ion and the extension of the original rectilinear path of the electron. Thus there is a limiting distance a determined by the electron speed v within which capture into a closed orbit occurs. For $v=0$ the initial path is a parabola and a becomes infinite since an infinitesimal dissipation of energy gives a closed orbit. The rate of recombination dN^+/dt is conveniently expressed in terms of the target area, $q(v)=\pi a^2$, since the number of effective collisions per cm^3 is

$$dN^+/dt = -vq(v)N^+N^- = -\alpha N^+N^- \qquad (1)$$

where the N's are concentrations of electrons and ions and α is called the recombination coefficient.

The energy radiated in recombination into a particular atomic level is the kinetic energy of the electron plus the negative energy, $h\nu_i$ of that level, where ν_i is the frequency of the corresponding series limit. This radiation takes place in a single act with emission of a quantum

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

Since the velocity will in general have a continuous range of values there will be a continuous spectrum extending toward higher frequencies beyond each series limit. The converse process is the absorption of light of frequency ν by an atom in the state of limiting frequency ν_i with consequent ionization of the atom by ejection of an electron with a velocity v. The variation of the absorption coefficient $k(\nu\nu_i)$ with ν in the continuous absorption beyond a series limit corresponds to the variation with electron speed of the capture area $q(v\nu_i)$ for capture into the level ν_i. If k is the atomic absorption coefficient (the absorption in one cm at a concentration of one atom per cm^3) then from the needle-quantum viewpoint it is a capture-area for quanta quite analogous to q for electrons.

The Einstein method of deriving the relation between these atomic functions is to set up the equations for the equilibrium in a black body inclosure at a temperature T, assuming that equilibrium holds for every pair of converse processes considered separately. There is then a necessary relation between $k(\nu\nu_i)$ and $q(v\nu_i)$ to satisfy the condition that both are purely atomic functions independent of temperature.[1]

$$q(v\nu_i)/k(\nu\nu_i) = 2ah^2\nu^2/m^2v^2c^2 \tag{3}$$

v and ν are related by Eq.(2) while a is the *a priori* probability of the state corresponding to ν_i (the number of magnetic levels) and c is the velocity of light. It is interesting that the right side of Eq.(3) is $2a$ times the ratio of the squares of the momenta of the quantum and the electron. As k is finite at the limit ν_i it follows from (3) that q must approach infinity for zero velocity as $1/v^2$ and the recombination coefficient $vq(v)$ will approach infinity as $1/v$.

CONTINUOUS ABSORPTION

As concerns the choice of experimental attack, a measurement of the atomic absorption coefficients is the simplest in principle. In practice, experiments are limited to the comparatively few normal energy levels which lie in the near ultra-violet or in the region of penetrating x-rays. These levels are the 1^2S levels of the alkalies, the K levels of nearly all elements, the L levels of elements heavier than iron, and the M levels beyond tungsten.

X-ray Absorption.[2] Measurements of the atomic absorption coefficient beyond the K limit for all elements and all wave-lengths can be approximately represented by a single formula. The absorption by the K shell is

$$k_K = 1.91 \times 10^{-2} Z^4 \lambda^3 \tag{4}$$

for wave-lengths less than the K limit and is zero for greater wave-lengths

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[1] Milne, Phil. Mag. **47**, 209 (1925). Becker and Kramers also published derivations of this relation at about the same time.

[2] A. H. Compton, X-Rays and Electrons; Van Nostrand Co., N. Y.

where Z is the atomic number and λ is the wave-length in cm. Similarly

$$k_L = 0.25 \times 10^{-2} Z^4 \lambda^3. \tag{4a}$$

With the approximation $\nu/R = Z^2/n^2$ where n is 1 for K and 2 for L the absorption of any element at the limits λ_K and λ_L is

$$k_K = 1.58 \times 10^{-12} \lambda_K \tag{5}$$

$$k_L = 0.83 \times 10^{-12} \lambda_L. \tag{5a}$$

There is evidence that the exponent of λ in (4) and (4*a*) is not exactly 3 but the departure is never great.

Continuous Absorption by Alkali Vapors. Numerous observations show that there is continuous absorption beyond the principal series limits but quantitative measurements have been unsatisfactory. The metal is usually vaporized in steel tubes with water-cooled ends so that estimates of vapor density are very uncertain. Harrison[3] found that the continuous absorption of sodium extended throughout the ultra-violet with a maximum at the principal series limit 2412A and concluded that a large and unknown proportion of this absorption was of molecular origin. Ditchburn[4] attempted to separate molecular and atomic effects in potassium by measuring line and continuous absorption at various pressures but without much success. The absorption at high pressures increased continuously beyond the limit while at lower pressures it decreased and then increased in going from the limit, 2856A toward shorter wave-lengths. From the low pressure curves he estimated k as 10^{-19} at the limit.

Boeckner and the author[5] have made a measurement of the absorption of caesium vapor at a comparatively low pressure, 0.1 mm, under equilibrium conditions but the observed absorption coefficient of 4×10^{-19} is subject to great uncertainty because of the low value of the total absorption. Recently Trumpy[6] has published relative measurements of absorption in sodium vapor shown in Fig. 1. A background of molecular origin is evident

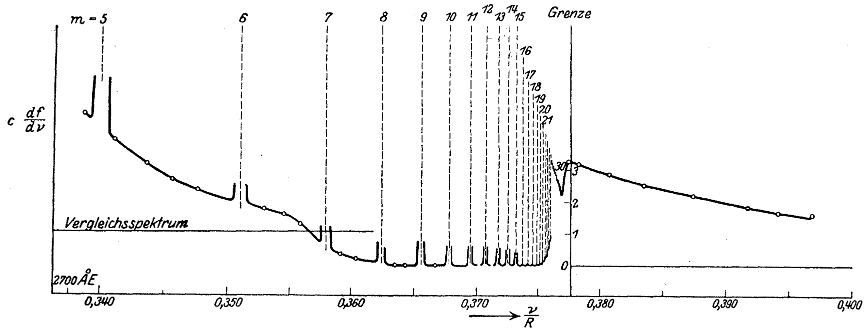

Fig. 1. Line and continuous absorption in sodium vapor (Trumpy). The wave-length scale extends from 2700A on the left to 2270A on the right with the limit at 2412.

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

[4] Ditchburn, Proc. Roy. Soc. **A117,** 486 (1928).

[5] Mohler and Boeckner, B. S. J. Res. **3,** 303 (1929).

[6] Trumpy, Zeits. f. Physik **47,** 804 (1928).

on the red side of the curve but is small near the limit so that he is justified in assuming that the absorption beyond the limit is atomic. This curve is much steeper than the λ^3 law of x-rays would give.

Line Absorption. Sugiura[7] has shown on theoretical grounds that in an absorption series the average value of the absorption coefficient over a definite frequency interval in the region of line absorption will approach in value the integral over an equal interval beyond the limit as we approach the limit. This offers a method of estimating the value of k at the limit which avoids the difficulty of molecular bands. The integral of $kd\nu$ across a line is difficult to measure and it is usually necessary to broaden the lines by high gas pressure or to use a thin layer at high vapor pressure to secure measurable magnitudes. Various results are given in the Handbuch der Physik[8] and in a recent paper by Waible[9] on series lines of caesium. If intervals $\Delta\nu$ are chosen equal to the average interval between lines to include one line in each interval, Waible's data for lines from the eighth to the fourteenth give

$$\int kd\nu/\Delta\nu = (0.48 \pm .01)\times 10^{-19} = k \text{ (limit)}. \tag{6}$$

Measurements of most other observers show a similar (but less accurate) constancy though there are differences of as much as ten-fold between different observers. Other results are given in Table I.

TABLE I. *Absorption coefficients at the 1S limit.*

Method	Caesium	Rubidium	Potassium	Sodium
Photo-ionization	2.3×10^{-19}	1.1×10^{-19}		
Continuous absorption	$4\ \times10^{-19}$		1×10^{-19}	
Line absorption	0.5×10^{-19}	$5\ \times10^{-19}$		8×10^{-19}
	$5\ \times10^{-19}$			
Recombination	0.5×10^{-19}			

PHOTO-IONIZATION

A direct measurement of k can be obtained from a measurement of the current I produced in an ionization chamber of length l by a beam of radiation of known energy flux $J(\nu)$. Since k is small

$$k(\nu) = Ih\nu/eNplJ(\nu) \tag{7}$$

where Np is the number of atoms per cm^3. The difficulty of avoiding surface effects has caused the development of other methods which give only relative values of k. One method[10] is to project a restricted jet of vapor through the ionization chamber; a second method[11] makes use of the neutralizing effect of positive ions on the negative space charge surrounding a hot wire cathode and the resulting electron current change to measure

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[7] Sugiura, J. de Physique **8**, 113 (1927).

[8] Wolf and Herzfeld, Handbuch der Physik vol. 20, p. 616.

[9] Waible, Zeits. f. Physik **53**, 459 (1929).

[10] Lawrence, Phil. Mag. **50**, 345 (1925), and Williamson, Proc. Nat. Acad. **14**, 793 (1928).

[11] Foote and Mohler, Phys. Rev. **26**, 195 (1925).

photo-ionization. The space-charge method offers the advantage of extreme sensitivity since the ratio of electron current change to ion current may be as high as 10^5.

Boeckner and the author[12] have recently studied several of the alkali vapors by both the space-charge method and the direct method. The current in a long ionization chamber with a cathode carefully shielded from light gave the absolute value at a favorable wave-length while measurements of the space-charge effect gave relative sensitivity as a function of wave-length. Radiation flux was measured directly by thermopiles. Fig. 2 shows results in caesium and rubidium. The ordinates give relative sensitivity which is proportional to $k/h\nu$. The caesium curve which has a maximum at the limit 3184A has been displaced to coincide with the rubidium limit at 2967A. The absolute values of k at the limits are for caesium $(2.3 \pm 0.2) \times 10^{-19}$ and for rubidium 1.1×10^{-19}. There are minor discrepancies between observers. Little[13] gives a caesium sensitivity much higher at the high-frequency end, while Lawrence and Edlefsen[14] give both caesium and rubidium curves like the rubidium curve of Fig. 2. They, as well as other observers, obtain quite different results in potassium. The curve drops from the limit 2856A, as in Fig. 2, and then increases beyond 2700 to a maximum three times as high as the limit near 2340. It is commonly accepted that the increase beyond the limit in potassium and caesium can be ascribed to molecules

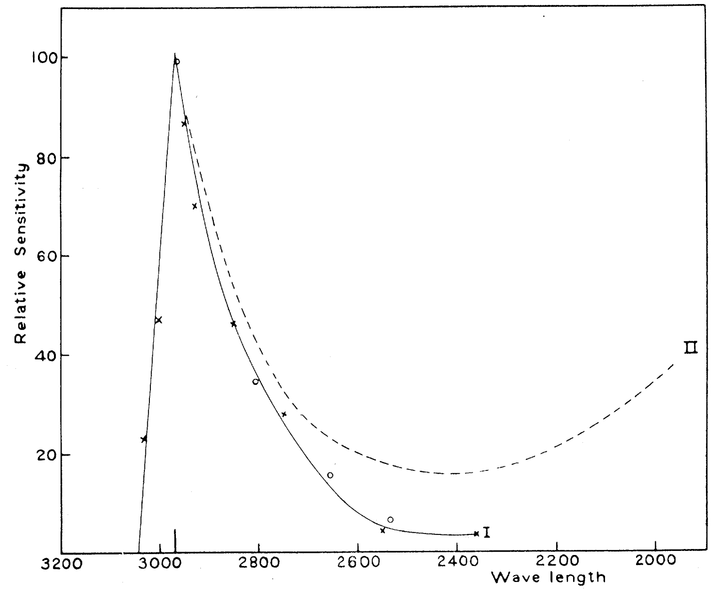

Fig. 2. Photoelectric sensitivity, I for rubidium and II for caesium. The caesium curve has been shifted to make the limit at 3184A coincide with the rubidium limit at 2967A.

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[12] Mohler and Boeckner, B. S. J. of Res. **3**, 303 (1929).

[13] Little, Phys. Rev. **30**, 109 (1927), and correction p. 963 (direct method).

[14] Lawrence and Edlefsen, Phys. Rev. **34**, 233 (1929) (space-charge method).

K_2 and Cs_2, though the shape of the curves does not change with pressure as might be expected on this hypothesis.

RECOMBINATION

With a notable exception measurements of the rate of disappearance of ions by recombination have been made at pressures comparable with an atmosphere under conditions such that the negative charges are heavy ions and not electrons. Results can be explained quantitatively on the basis of a theory of Thompson that recombination is effected by a three-body collision in which a neutral molecule takes up the excess energy;[15] so the experiments have little bearing on the problem of spontaneous recombination. Various lines of evidence indicate that under most low-pressure discharge conditions recombination in free space is negligible compared to loss of ions by diffusion to walls and electrodes.[16]

Recombination Spectra. The continuous spectra predicted by Eq.(2) give a safe criterion for the occurrence of spontaneous recombination and there are several striking instances of such spectra. Balasse[17] finds continuous spectra near the center of powerful induction ring discharges in caesium, potassium, mercury, and cadmium; while Herzberg[18] under similar conditions has photographed a continuous band beyond the Balmer series of hydrogen. Paschen[19] has observed recombination bands in a hollow cathode discharge in helium while the author has obtained such spectra in thermionic discharges at moderately high pressure and current.[20] These spectra are characterized by abnormally high intensity of higher series lines. The lines which are much broadened by high ion concentration merge into the continuous background which extends without any discontinuity through the limit and far to the violet side. The relative intensity in the series as well as the lines is abnormal. Thus in mercury and helium the triplet series are much stronger than the singlets. This may be ascribed to the higher *a priori* probability of triplet terms in accord with Eq. (3). Fig. 3 gives curves of intensity distribution of the continuous spectrum in caesium[20] and in helium.[21]

On the basis of considerations given in the introduction it is probable that low electron speed (small potential gradient) is more essential than high ion concentration for conspicuous recombination. An analysis of conditions in the thermionic discharges bears this out. The discharge tube consists of a hairpin cathode near the axis of a cylindrical anode and the voltage drop is within a thin bright sheath around the cathode. The recombination light in caesium appears as a diffuse yellow glow extending from the cathode toward

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[15] Loeb, Kinetic Theory of Gases; McGraw Hill and Co.: Marshall; Phys. Rev. **34,** 618 (1929).

[16] Seeliger, Phys. Zeits. **30,** 329 (1929) in a very complete summary of recombination experiments includes a critique of negative results.

[17] Balasse, Comptes rendus **184,** 1002 and 1320 (1927).

[18] Herzberg, Ann. d. Physik **84,** 565 (1927).

[19] Paschen, Berl. Ber. p. 135 (1926).

[20] Mohler, Phys. Rev. **31,** 187 (1928).

[21] Mohler and Boeckner, Bur. Stds. J. of Res. **2,** 489 (1929).

the anode, and probe measurements[21] show that this region is characterized by high ion concentration (10^{12} to 10^{14} per cm^3) and very low electron speeds (0.1 to 0.4 volts). The space is slightly positive with respect to the anode so that slow electrons are entrapped to maintain a concentration nearly equal to that of the positive ions.[22]

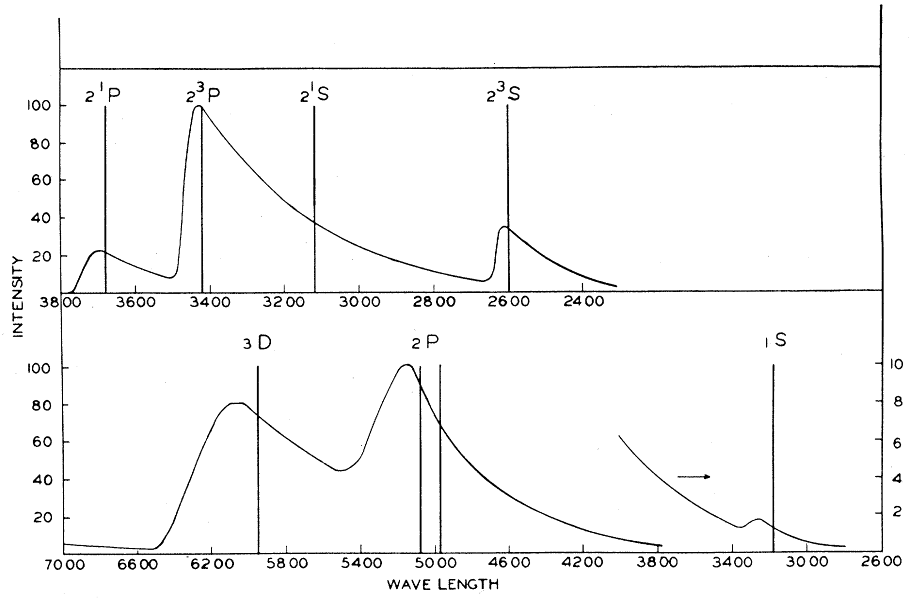

Fig. 3. Intensity distribution in the continuous emission spectrum of helium (upper curve) and caesium (lower curve).

Recombination in the Afterglow. Lord Rayleigh[23] has observed spectra indicative of recombination in the luminous vapor drawn from the discharge space in a mercury arc. Webb and Wang[24] find by probe measurements that the atomic radiation under these conditions is dependent on the presence of ions and very slow electrons, which have lost their speed in the course of diffusion. Miss Hayner[25] has studied the afterglow of mercury with a high speed sectored disk and commutator and finds that most lines fall to nearly zero intensity in 10^{-4} sec. after cutting off the voltage. But some lines (notably higher series lines of the diffuse triplets) then rise in intensity reaching a maximum about 3×10^{-4} sec. after the cutoff before finally fading. Her hypothesis that recombination is small at first and rapidly increases as the electrons lose their speed is supported by similar experiments of Kenty[26] in an argon discharge. By means of a suitable commutator he was able to make probe measurements at selected intervals during the dark period and afterglow. The electron speed dropped in about 2×10^{-4} sec. (the dark period) to

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[22] Langmuir, Phys. Rev. **33**, 954 (1929).

[23] Rayleigh, Proc. Roy. Soc. **A108**, 262 (1925).

[24] Webb and Wang, Phys. Rev. **33**, 329 (1929).

[25] Hayner, Zeits. f. Physik **35**, 365 (1926).

[26] Kenty, Phys. Rev. **32**, 624 (1928).

0.4 volts and remained nearly the same for the duration of the afterglow (2×10^{-3} sec.). An accelerating voltage for electrons applied after the cutoff quenched the afterglow, though if the voltage was small enough the electron concentration was actually increased. This indicates that loss by recombination predominates over diffusion loss and his measurements of the rate of change of concentration give a value of the total rate of recombination which is certainly reliable as to order of magnitude. The electron concentration dropped from 7×10^{12} to 2×10^{12} in the interval from 2.5×10^{-4} to 2.5×10^{-3} sec. after the cutoff. Assuming $N^+=N^-$, Eq. (1) gives $\alpha=2\times10^{-10}$ for 0.4 volt electrons or $q=5\times10^{-18}$ cm^2.

Measurements of the Recombination Radiation.[21] The intensity $J(\nu)d\nu$ in a continuous band at a given frequency interval beyond the limit depends on the concentration of electrons of the corresponding speed, on the concentration of ions, and on the recombination coefficient for capture into the level concerned. Since the number of quanta emitted in unit volume equals the number of recombinations, we have corresponding to Eq. (1)

$$J(\nu)d\nu/h\nu=vq(v\nu_i)N^+N^-F(v)dv \tag{8}$$

where $F(v)dv$ gives the fraction of the electrons in a range corresponding to $d\nu$ (Eq. 2).

Probe measurements show that the electron velocities in a thermionic discharge under recombination conditions have a strictly Maxwellian distribution about an average energy that can be accurately determined. Measurements of the spectral intensity of the radiation in the vicinity of the probe combined with the electrical measurements thus give relative values of $vq(v\nu_i)$ as a function of ν or v with a precision quite independent of uncertainties in N^+ and N^-. Figs. 4, 5, and 6 illustrate the experimental data and the computed curve for the band beyond the $2P$ limit of caesium. The two sets of measurements were made under quite different conditions of vapor pressure and ion concentration, yet the form of the vq curve remains the same. The curve of Fig. 6 is a plot of the equation

$$vq(v,2P)=k_1/\nu^2(\nu-\nu_i)^{1/2}. \tag{9}$$

Less accurate measurements on the band beyond the $3D$ limit of caesium fit the same curve. The maximum intensity at the $1S$ limit is about one percent of that at $2P$. At comparatively low intensities $J(\nu)$ is roughly proportional to the square of the discharge current or the square of the ion current to the probe. This is in accord with Eq. (8) if we assume that $N^+=N^-$; and on the basis of the ion current a rough estimate can be made of the numerical values of the concentrations. The data of Set II, Figs. 4 and 5 give the effective collision area for capture of 0.2 volt electrons into $2P$ as 6×10^{-21} cm^2, while for $1S$ the area is 1.5×10^{-23} cm^2. This is very much smaller than the total capture area found by Kenty for argon ions and 0.4 volt electrons ($q=5\times10^{-18}$ cm^2), and it seems probable that most of the recombination takes place into outer energy levels giving infra-red radiation. The great intensity of higher series lines supports this interpretation.

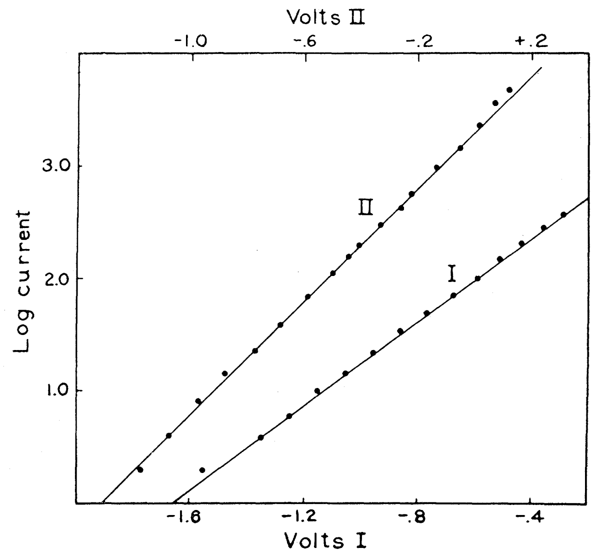

Fig. 4. Electron velocity distribution curves for two conditions of the caesium discharge. I gives an average electron energy of 0.345 volts; II gives 0.281 volts.

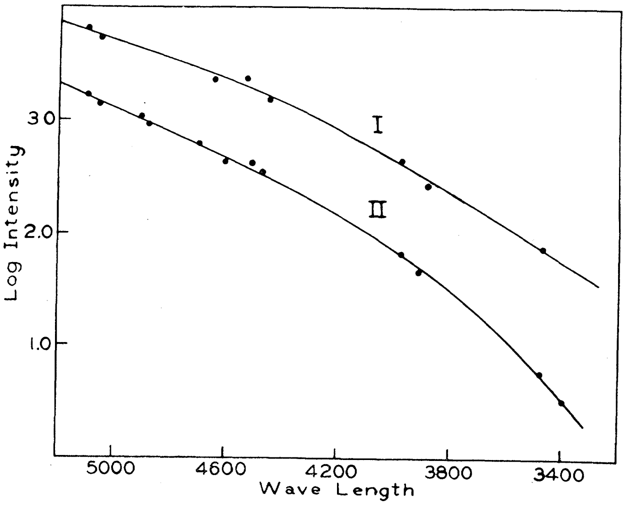

Fig. 5. Intensity distribution in the $2P$ band of caesium under conditions giving curves I and II of Fig. 4.

SUMMARY OF RESULTS

On the basis of the x-ray law of absorption and Eq. (3), the law of variation of capture area is

$$q = c_1/\nu(\nu-\nu_i) = c_2/\nu v^2 \tag{10}$$

while from Eq. (9) based on intensity distribution in the caesium $2P$ band we have

$$q = c_1/\nu^2(\nu-\nu_i) = c_2/\nu^2 v^2 \tag{11}$$

where the c's are constants. The difference in form is small near the limit where the factor involving v is predominant. Conversely applying Eq. (3) to Eq. (11) we find that $k(\nu, 2P)$ is proportional to λ^4 instead of λ^3. It is important that the empirical Eq. (11) conforms to the requirement that k remains finite at the limit.

Fig. 7 gives the variation of k as derived from various sources. The curves for $1S$ levels of alkalies (potassium, as well as those plotted) fall close together near the limit and depart extremely from the x-ray law, while the absorption of caesium atoms in the $2P$ and $3D$ states is much like that of x-ray levels.

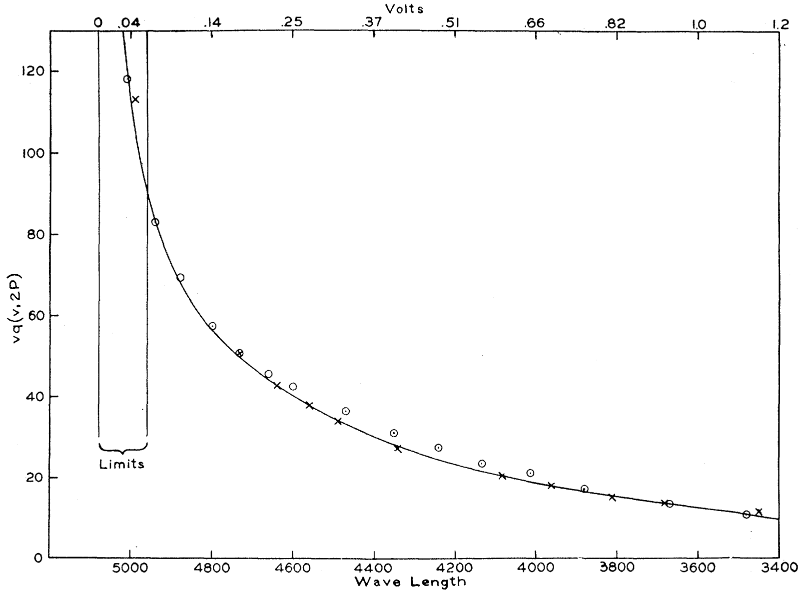

Fig. 6. Relative values of the coefficient for recombination into $2P$ from data of Figs. 4 and 5. Crosses refer to set I and circles to set II.

From the capture areas as given in the last section we derive by Eq. (3) that k for caesium atoms in the $2P$ state is 3×10^{-17} and for the normal $1S$ state is 0.5×10^{-19}. In view of the experimental uncertainties the latter value is in satisfactory agreement with other estimates. Table I summarizes the estimates of k for the alkalies covered in this paper. The values derived from direct measurement of photo-ionization are probably the most reliable.

Various theoretical derivations of the continuous absorption of hydrogenic atoms based on classical and correspondence principle considerations[27] lead to a λ^3 law of absorption. Wave mechanics derivations[28] show that the simple power law is only an approximation. Thus Oppenheimer finds for hydrogen in the 2_1 state that

$$k=0.91\times10^{-12}\lambda^{2.9}/\lambda_i^{1.9}$$

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[27] Kramers, Phil. Mag. **46,** 836 (1923).

[28] Oppenheimer, Zeits. f. Physik **41,** 268 (1927).

near the limit and that the exponent of λ approaches 3.5 for high frequency; while for the 2_2 state

$$k = 1.0 \times 10^{-12} \lambda^{3.4} / \lambda_i^{2.4} \tag{12a}$$

$$k \text{ (limit)} = 1.0 \times 10^{-12} \lambda \text{ (limit)} \tag{12b}$$

where wave-lengths are in cm. At the Balmer limit (3646A) $k(2_2) = 3.6 \times 10^{-17}$. This is of the same form and in close numerical agreement with the Eqs. (5) and (5a) for x-ray absorption. The formula for K absorption gives $k = 5.8 \times 10^{-17}$ at 3646, while the L series Eq. (5a) gives 3.0×10^{-17}. The estimate of k for caesium atoms in the $2P$ state was also 3×10^{-17} (12b would give 5×10^{-17} at $\lambda = 5000$).

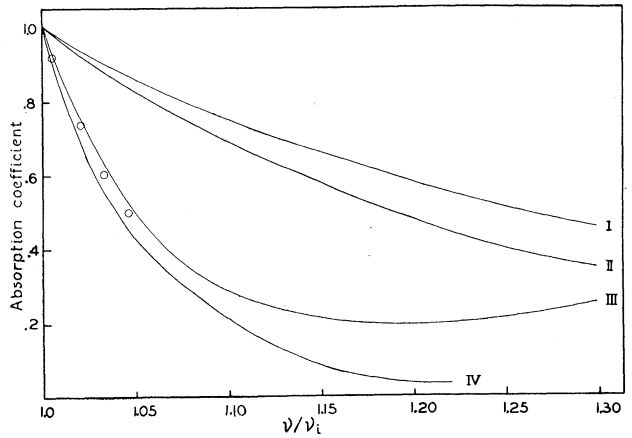

Fig. 7. Change of absorption coefficient with frequency. I from x-ray law, II from recombination into $2P$ of caesium, III from photo-ionization of caesium, IV from photo-ionization of rubidium. Circles from absorption of sodium (Fig. 1).

We have the striking result that the absorption curve for caesium atoms in the $2P$ and $3D$ states is closely hydrogenic both in magnitude and shape, while the $1S$ level departs widely from hydrogen in both respects. This anomaly can be partially understood. Dispersion and absorption theories (including wave mechanics) generally make use of the assumption that the integral of the absorption coefficient over all frequencies is for a single electron system equal to the absorption of a classical oscillator. Experiments on the alkalies show that, in contrast with hydrogenic atoms, nearly all this absorption is in the first line.[29] Consequently the absorption in the higher lines and beyond the limit must be correspondingly diminished. Sugiura[30] has carried out approximate computations by wave mechanics methods for the line absorption of sodium which are in satisfactory agreement with experimental values. Attempts by Hargreaves[31] and Trumpy[32] to extend such

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[29] Wolf and Herzfeld, Handbuch der Physik, Vol. 20.

[30] Sugiura, Phil. Mag. **4**, 495 (1927).

[31] Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1929).

[32] Trumpy, Zeits. f. Physik **54**, 372 (1929).

computations to the continuous absorption of lithium give curves which are not in mutual agreement and are quite unlike the experimental curves for heavier alkalies. The former gives a curve which reaches a maximum slightly beyond the limit and falls off roughly as λ^3, while the latter derives a curve which drops from the limit at a similar rate.

Experiments give a range of from 10^{-19} to over 10^{-17} for continuous absorption coefficients of atoms in various states, and theoretical considerations indicate that 5×10^{-17} is about the maximum for any limit in the visible or near ultra-violet. It follows that the area for capture into any level can not be much greater than that estimated for $2P$ of caesium (6×10^{-21} cm^2 for 0.2 volt electrons). This area is of a different order of magnitude from atomic dimensions (the cross section of the caesium ion is about 10^{-15} cm^2) so that the mechanical picture of the recombination process can only be accepted with reservations. The fact that under various discharge conditions recombination radiation becomes appreciable, in spite of these small magnitudes, is explained by the phenomenon of plasma formation.[22] The entrapping of slow electrons and consequent reduction of potential gradient in regions of high ion concentration brings about spontaneously a condition that is ideal for the experiment.