

## PHOTOIONIZATION PROBABILITIES OF ATOMIC POTASSIUM

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## ABSTRACT

Calculations of the absorption probabilities in the continuous spectrum of the potassium atom were made to investigate the possibility that the second maximum in the experimental photoionization curve is of atomic origin. The model for the  $K$  atom is a single normal state valence electron moving in a non-Coulomb central force field. Two fields were used. The first was determined to satisfy the quantum conditions on the radial phase integrals for the x-ray and optical levels. This field is in error in the region of the deeper shells, and was replaced by Hartree's self-consistent field for the  $K$  atom, corrected for polarization of the core to give the observed term values for the normal state and  $3s$  orbits as eigenvalues of the wave equation. The wave functions were obtained by numerical integration, and the matrix integrals for transition probabilities determined graphically. The resulting probability curve was found to decrease steadily from the series limit, with no hint of the experimental maximum. It further appears that no reasonable changes in the field will produce such a variation. The magnitude of the absorption coefficient at the series limit is about  $2 \times 10^{-20}$  by our calculations, and

$$-df/d\epsilon = 1/3 \nu/R [I]^2,$$

where  $I$  is the matrix integral, is 0.0024, much smaller than for lighter hydrogen-like atoms. From the percentage association of the vapor and  $-df/d\epsilon$  for the atom it is estimated that the second maximum could be attributed to molecules if  $-df/d\epsilon$  per valence electron at the molecular threshold were about 2. This value seems very large, but not impossibly so.

THE photoionization per unit light intensity in potassium vapor as a function of the frequency of incident radiation shows two maxima,<sup>1</sup> one at the series limit, 2856Å, and another at 2340Å. The number of molecules present in the  $K$  vapor under the conditions of the observations was not very large, and it has seemed probable that the observed absorption was due to atomic  $K$ . If this were so the course of the absorption coefficient for the  $K$  atom would be very different from that of hydrogen or any other alkali atom, for except in the case of  $K$  the absorption falls off rapidly and steadily from the limit. It seemed of interest to determine whether this anomalous behavior could be understood theoretically. We have therefore calculated the absorption coefficient quantum mechanically, taking as a model for the  $K$  atom a single valence electron moving in a suitably chosen non-Coulomb field. Calculations similar in some respects to ours have been made earlier for other alkali atoms. Thus Hargreaves<sup>2</sup> determined relative intensities in the continuous spectrum of lithium, using the central field of Hartree, with numerical and graphical integration. During the progress of this work calculations by Trumphy<sup>3</sup> for lithium and sodium have appeared.

<sup>1</sup> Lawrence and Edlefsen, Phys. Rev. **34**, 1056 (1929).

<sup>2</sup> Hargreaves, Cambr. Phil. Soc. **XXV**, 75 (1929).

<sup>3</sup> Trumphy, Zeits. f. Physik **71**, 720 (1931).

We have used two methods to determine the field in which the valence electron of our atom moves, in both of which the core electrons are taken into account only by the addition of their field to the field of the nucleus. One is

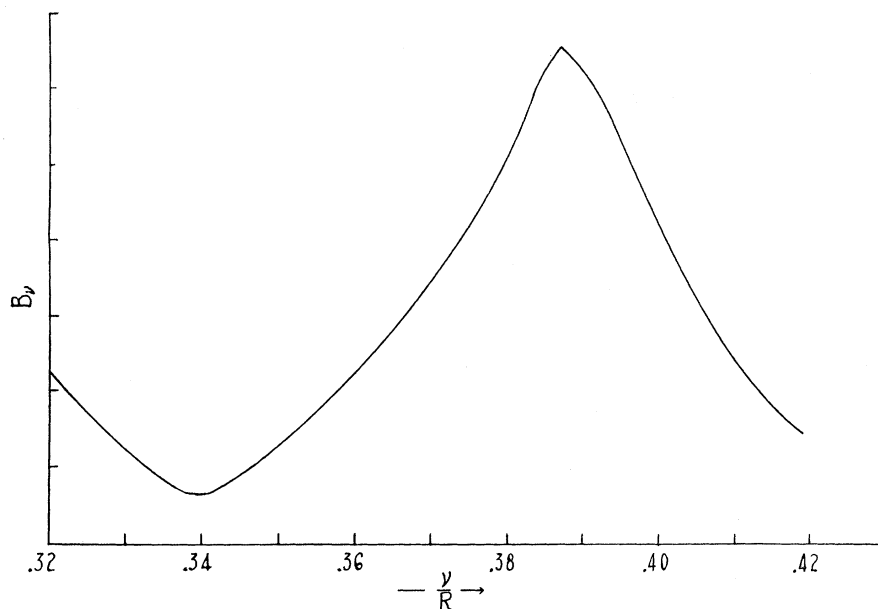


Fig. 1. Relative ionization probability,  $B_v$ , of potassium vapor as a function of the frequency as obtained by Lawrence and Edlefsen. 0.32 is the term value for the normal state, and thus the, frequency of the series limit in units of  $R$ .

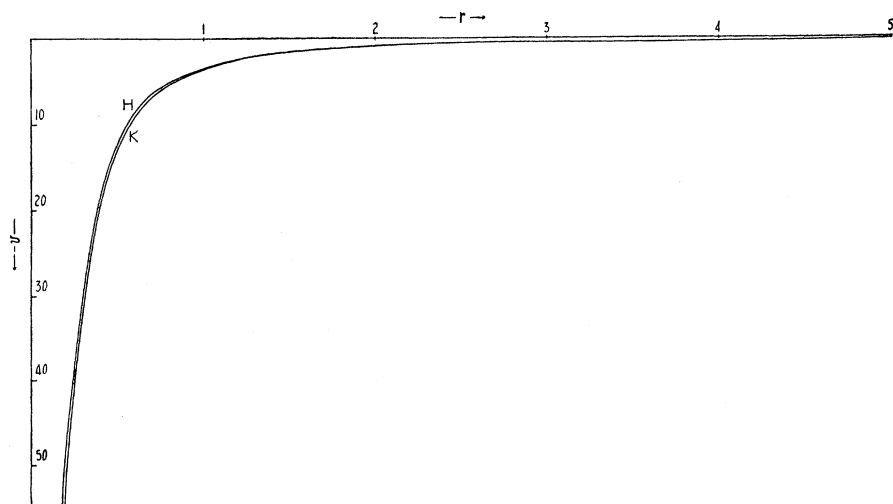


Fig. 2. Fields representing the  $K$  ion. Curve  $K$  was obtained by the phase integral method. Curve  $H$  is the Hartree self-consistent field, corrected for polarization of the core.  $r$  is in units of  $a_0$ .

substantially that applied by Zwaan<sup>4</sup> to the computation of the line intensities of Ca<sup>+</sup>. In this method the field is so chosen that the radial phase integrals have the proper half integral values when the corresponding experimental term values are given to the energy. In the second method we started with the self-consistent field for the *K* ion; for this we are greatly indebted to Dr. Hartree, who communicated his values to us. This field we adjusted to give the correct term values for the normal state and the 3<sub>3</sub> orbit, by a theoretically derived correction for the polarization of the core. We shall discuss these two methods in order, and shall return later to a consideration of the possible error in our determination of the field, and its effect upon the absorption coefficient. The two fields differ appreciably, but they give approximately the same absorption curve; in both cases the absorption decreases steadily from the limit, and thus fails to agree with the experimental results.

It is convenient to work with "atomic units", which are defined:

Unit of length,  $a_0 = h^2/4\pi^2me^2$ , radius of the first Bohr orbit of hydrogen.

Unit of energy,  $E_0 = e^2/2a_0$ , equal to the ionization potential of the *H* atom with a fixed nucleus. This is one half the unit adopted by Hartree.<sup>5</sup>

Unit of time,  $1/4\pi cR$ .

Then  $-E = \epsilon E_0$ ,  $V(r) = v(r)E_0$ , and  $r$  is expressed in terms of  $a_0$ .

For the first method we proceed as follows: The Kramers phase integral with these units is

$$n - 1 - \frac{1}{2} = \frac{1}{\pi} \int_{r_{\max}}^{r_{\max}} \frac{1}{r} (-\epsilon r^2 - (l - \frac{1}{2})^2 - r^2 v(r))^{1/2} dr.$$

The field is determined graphically, using in this expression the empirical values of  $\epsilon$  for each level in turn, with the proper quantum numbers. Values for the x-ray terms were obtained from Siegbahn's tables, or from the Moseley diagrams. Fine structure differences were neglected and a mean value taken for multiplet terms. Data for the optical levels were those given by Paschen and Goetze. For each orbit  $\epsilon r^2 + (1 + \frac{1}{2})^2$  is a parabola, and an initial  $v r^2$  curve is assumed, to be varied until the integral, evaluated by means of a planimeter, is as nearly  $(n - 1 - \frac{1}{2})$  in every case as possible. In thus attempting to satisfy simultaneously the quantum conditions for all the terms it is assumed that the field is the same no matter from which shell an electron is missing. The error introduced by this assumption could amount to almost a whole unit of charge for the inner shells, since the charge density of the valence electron near the nucleus is small compared with one belonging to the *K* or *L* group. When the curve of calculated intensities failed to reveal the experimental maximum the Kramers field was abandoned in favor of the self-consistent field of Hartree; for small radii, however, it serves as a lower limit to variations possible in the field, as will be explained later.

In the self-consistent field the actual field of every electron is represented by the field of its mean charge distribution. Such a field does not take into

<sup>4</sup> Zwaan, Doctor's Dissertation, Utrecht, 1929.

<sup>5</sup> Hartree, *Cambr. Phil. Soc. Proc.* **XXIV**, 19 (1928).

account the polarization of the core by the valence electron, and in the case of  $K$  the ionic field given by Hartree fails entirely to give the observed term value for the normal state. For large radii we may introduce a polarization correction by subtracting from the potential  $\alpha e^2/r^4$ , where  $\alpha$  is the polarizability of the core,  $0.8 \times 10^{-24}$  for  $K$ . This correction was made directly for  $r > 3a_0$ ; in the region  $r < 0.8a_0$  the Hartree curve was left unchanged; in the intermediate range  $0.8a_0 < r < 3a_0$  the Hartree curve was so lowered that it joins the other portions smoothly, and that it gives, on numerical integration of the wave equation, the experimental term value for the normal state and very nearly that for the  $3s$  orbit.

The radial factor of the wave function satisfies the equation:

$$\chi'' + \frac{2}{r} \chi' + \left( v - \epsilon - \frac{l(l+1)}{r^2} \right) \chi = 0.$$

If we write  $P = r\chi$ , the equation for  $P$  is

$$P'' + (v - \epsilon - l(l+1)/r^2)P = 0.$$

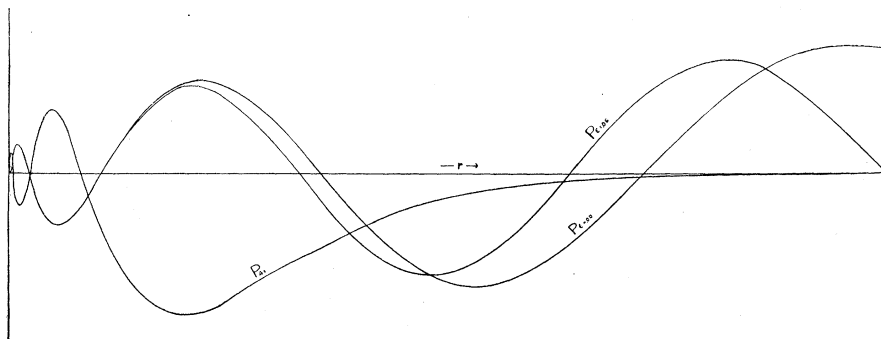


Fig. 3. Wave functions for the normal state,  $4_1$ , and two points in the continuum:  $\epsilon=0$ ,  $\epsilon=-0.06$ . The range of  $r$  in the diagram is  $21 a_0$ .

The observed term value for the normal state ( $4_1$  orbit) is 0.32, and  $l=0$ . The general method for determining wave functions was numerical integration,<sup>6</sup> starting from a series solution of the equation with  $v = 38/r$  very near  $r=0$ , but approximations suggested by Kramers<sup>7</sup> served for comparison and checking; at large  $r$  the analytic solution for a Coulomb field was used, being fitted on smoothly to the curve at a point beyond which it was justified. The maxima and nodes of the normal state wave function are almost independent of reasonable changes of the field, ( $0.8a_0 < r < 3a_0$ ), but the term value determines the point of inflection, so that the requirement that the function approach zero asymptotically for a given eigen energy gives a sensitive check on the field. Such a field is not unique, but, starting with Hartree's determination and keeping the condition on the phase integrals satisfied, a polarization correction is fairly well defined.

<sup>6</sup> See reference 5.

<sup>7</sup> See reference 4.

For transitions to the continuous spectrum of energy values we must have  $l=1$ , to satisfy the selection rule. The wave equation becomes

$$P'' + (v - \epsilon - 2/r^2)P = 0$$

where  $-\epsilon$  is now positive. The wave function is oscillatory, and the solutions of the asymptotic form,  $P'' - \epsilon P = 0$ , are circular functions. The solution is chosen which is zero at  $r=0$ , and behaves there as  $r^{l+1}$ . The wave functions are found by numerical integration throughout the region in which there is a contribution to the matrix integrals.

The normal state function is normalized in the usual fashion, by determining graphically  $\int_0^\infty P^2 dr$ , but normalization in the continuous case is more troublesome. Hargreaves shows that the normalized solution is

$$\frac{1}{\pi^{1/2}\epsilon^{1/4}} \frac{aL + bM}{(a^2 + b^2)^{1/2}}$$

with

$$L = \frac{\alpha G - \beta H}{2}, \quad M = \frac{\alpha H + \beta G}{2}.$$

Here

$$\alpha + i\beta = \epsilon\Gamma(2 + \epsilon^{1/2})\exp(-i\epsilon^{1/2}\pi/2)$$

and  $G$  and  $H$  are power series solutions of the equation  $P'' + (2/r - \epsilon - 2/r^2)P = 0$ .

$$G = \sigma^2(a_0 + a_1\sigma + a_2\sigma^2 + a_3\sigma^3 + \dots)$$

$$H = \frac{1}{\sigma}(b_0 + b_1\sigma + b_2\sigma^2 + b_3\sigma^3 + \dots) + cG(\sigma) \log \sigma$$

with  $\sigma = 2r$ .

In practice  $G, H, G', H'$ , were evaluated<sup>8</sup> for the point nearest the origin at which the field may be assumed Coulomb,  $\alpha$  and  $\beta$  calculated, and thus  $L, M, L', M'$ , determined. These were fitted onto the values of  $P$  and  $P'$  obtained by numerical integration at that radius by means of determining  $a$  and  $b$  in

$$\frac{1}{\pi^{1/2}\epsilon^{1/4}} \frac{aL + bM}{(a^2 + b^2)^{1/2}}.$$

It is obvious that this method fails for  $\epsilon=0$ . The normalized solution<sup>9</sup> for this case is

$$(1/2)^{1/2} \frac{aG_1 + bH_1}{(a^2 + b^2)^{1/2}}$$

$$G_1 = \sigma^{1/2}J_3(2\sigma^{1/2})$$

$$H_1 = \sigma^{1/2}Y_3(2\sigma^{1/2})$$

<sup>8</sup> I wish to thank Mr. R. Edwin Worley for his assistance in the computation of these series.

<sup>9</sup> Hartree, *Cambr. Phil. Soc. Proc.* **XXIV**, 430 (1928).

$J$  is the ordinary Bessel function and  $Y$  is Neumann's Bessel function of the second kind:

$$J_3(2\sigma^{1/2}) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!(n+3)!} \sigma^{3+2n/2}$$

$$Y_3(2\sigma^{1/2}) = \frac{2}{\pi} J_3(2\sigma^{1/2}) \log \sigma^{1/2} - \frac{1}{\pi} \sum_{n=0}^{\infty} (-1)^n \frac{\psi(n) + \psi(3+n)}{n!(3+n)!} \sigma^{(3+2n)/2}$$

$$- \frac{1}{\pi} \sum_{n=0}^2 \frac{(2-n)!}{n!} \sigma^{(2n-3)/2}$$

where  $\psi(n) = -0.0557216 + 1 + \frac{1}{2} + \dots + 1/n$ .

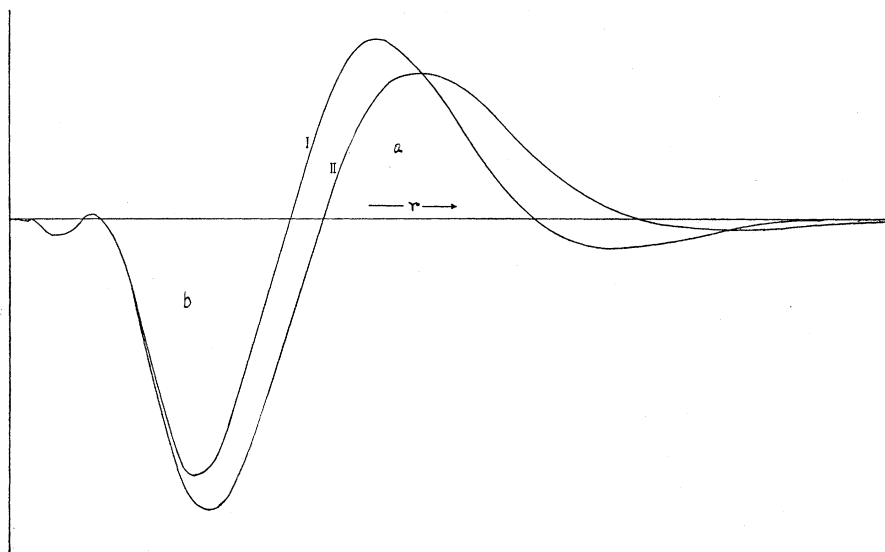


Fig. 4. Plot of  $rP_{4_1}P_{-\epsilon}dr$  as a function of  $r$ . Curve I is for  $\epsilon = -0.06$ , and curve II for  $\epsilon = 0$ . Again the range of  $r$  is  $21a_0$ .

A value of  $r$  may be chosen for which  $2\sigma^{1/2}$  is an integer, and values of  $J$  and  $Y$  obtained from tables of Bessel functions.  $J'$  and  $Y'$  are determined by their relations to the functions of adjacent order.

The absorption coefficient<sup>10</sup> is given by

$$\sigma = \frac{8\pi^3 e^2 \nu}{3hc} \frac{\left[ \int_0^\infty r P_{4_1} P_{-\epsilon} dr \right]^2}{\left[ \int_0^\infty P_{4_1}^2 dr \right]^2} = \frac{8\pi^3 e^2 \nu}{3hc} (I)^2$$

where  $P_{-\epsilon}$  is normalized as above. The coefficient was computed for four values of  $\epsilon$ :  $\epsilon = 0$ , the series limit,  $\epsilon = -0.02$ , corresponding to the minimum

<sup>10</sup> See reference 2.

of the experimental curve,  $\epsilon = -0.06$ , its maximum, and  $\epsilon = -0.10$ . The resulting curve of probabilities falls off monotonically from the series limit, as shown by Fig. 5, somewhat faster than the  $\lambda^3$  law, and exhibits no suggestion of the experimental peak. Calculations made earlier with the Kramers field gave a curve of much the same form. The absolute value of the atomic absorption cross-section at the series limit is about  $2.2 \times 10^{-20}$ , while Mohler<sup>11</sup> gives  $1 \times 10^{-19}$  from estimations on Ditchburn's experiments, and  $8 \times 10^{-19}$  as that for sodium. The values of  $-df/d\epsilon = \nu(I)^2/3R$  at the series limits for the hydrogen-like atoms are:

H (Sugiura) <sup>12</sup>	0.8
Li (Trumpy)	0.46
Na (Trumpy)	0.038
K	0.0024.

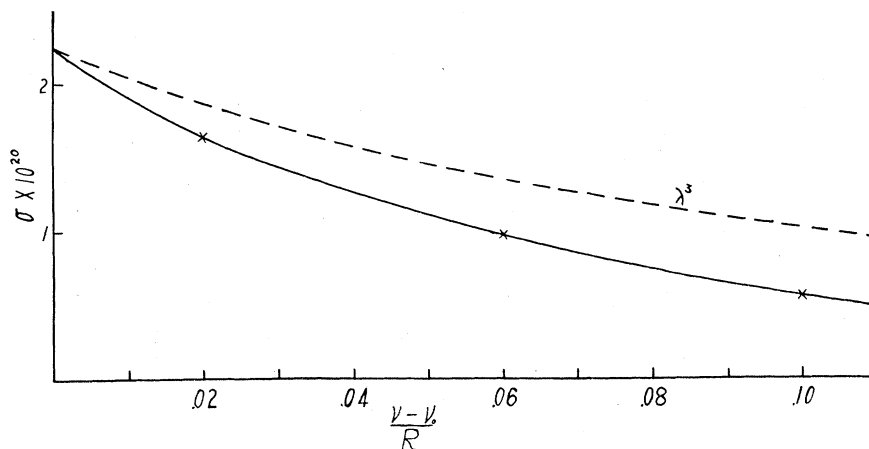


Fig. 5. Absorption coefficient as a function of frequency. The initial point and the three crosses represent calculated points, and the dotted curve shows the  $\lambda^3$  law.

We now examine the field of the atom to find whether any possible changes will give the anomalous intensity maximum. It may again be divided into three parts. For  $r > 5a_0$  it is fixed, being, except for  $\alpha e^2/r^4$ , very nearly Coulomb. For  $r < a_0/2$  Hartree's field should be a good approximation, and any polarization effect would not bring it lower than the Kramers field, which, as we saw, also gave a decreasing curve of intensities. In the range  $a_0/2 < r < 5a_0$  the field is not precisely determinate, but we have examined the effect of changes in this region in some detail. In the first place the nodes of the wave functions in the continuum (see Fig. 3) will for any field move in with an increase of energy. From the plot of the matrix integrals (Fig. 4) we see that the two regions  $a$  and  $b$  nearly cancel each other; for our field  $b$  is the larger. In order that an increase in energy should increase the absorption coefficient it would therefore be necessary: (1) that  $a$  be larger than  $b$  for small energies;

<sup>11</sup> Mohler, Phys. Rev. Suppl. 1, 219 (1929).

<sup>12</sup> Sugiura, Jour. de Phys. VIII, 113 (1927).

or, (2) that the absolute magnitude of the normalized wave functions for the continuum should increase rapidly with the energy. We have convinced ourselves that no change which leaves correct the term value of the normal state can give a field satisfying condition (1); that is to say, it is impossible to change the field in the region  $a_0/2 < r < 5a_0$  in such a way that the nodes are moved out appreciably and that the point of inflection of the normal state wave function remains in place. As to (2) we may say that for both the fields for which we have made calculations the magnitude of the continuous wave function decreases markedly and uniformly with increasing energy; we see no reason why an electron of energy 0.04, say, should spend a relatively very much larger time in the atom than one of energy 0.02. The analysis involved in the normalization of the continuous wave functions is, however, highly complicated, and we have not been able to exclude with complete rigor the occurrence of such anomalous behavior as suggested in (2).

We have seen that the absorption coefficient falls monotonically from the limit, and that its magnitude there is approximately  $2 \times 10^{-20}$ . It also appears that no reasonable changes in the atomic field will yield such a variation of the coefficient with the frequency as is shown in the experimental curve. It has been suggested by some authors that the second maximum is due to molecular ionization. According to calculations by Loomis and Nusbaum<sup>13</sup> of the percentage of association from the spectroscopically determined heat of dissociation, the ratio of molecules to atoms at 210°C, the temperature at which Lawrence and Edlefsen worked, is 2:1000. Their maximum could then be explained as a molecular phenomenon if  $df/d\epsilon$  for the molecules at the threshold is approximately 2, as compared to the atomic  $df/d\epsilon$  of 0.0024. This value, while not impossible, seems unreasonably large. Experiments are in progress in this laboratory to determine the velocities of the emitted electrons, and to find whether there is any dependence of the relative heights of the maxima on temperature, which should furnish a conclusive answer to the question.

The writer wishes to thank Professor H. A. Kramers for suggestions at the beginning of work on this problem, and to express appreciation of the advice and encouragement of Professor J. R. Oppenheimer, under whose supervision the investigation was carried out.

<sup>13</sup> Loomis and Nusbaum, *Phys. Rev.* **39**, 89 (1932).