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THE PHOTO-IONIZATION OF POTASSIUM VAPOR

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ABSTRACT

Using a space-charge-neutralization method described in a recent publication the variation with wave-length of the ionization per unit light intensity B_ν in potassium vapor has been studied. B_ν exhibits maxima in the range 2100A to 3000A, one at the series limit, 2856A, and another at 2340A, the magnitude of the latter maximum being three times the former. A minimum value of B_ν occurs close to 2700A. Former results are shown to agree with the present much more accurate data though, because of the wide bands of wave-lengths used and the scantiness of observations, the earlier work failed to reveal the salient features here presented. The decrease of the ionization efficiency on both sides of the series limit is similar to the corresponding variation in caesium and rubidium and it seems probable, though not here proved, that the ionization by wave-lengths longer than the series limit is due to absorption of principal series lines. The increase of B_ν beyond the series limit has been attributed in the past to ionization of molecules. The present work shows that on this view the apparent molecular threshold occurs at 2700A and not at 2550A as estimated from earlier work. This fact in itself constitutes a serious objection to interpreting the observed variation of B_ν as a molecular phenomenon. It is pointed out that Williamson's observations of the emergent velocities of the photo-electrons show no evidence of molecular ionization involving dissociation of the molecule and ionization of one of the atoms. Also Ditchburn's observations of the continuous optical absorption due to potassium atoms agree qualitatively with the present results. It thereby appears probable that the observed dependence on wave-length of B_ν is an atomic property of potassium.

IT HAS been shown[1,2] that the photo-ionization per unit light intensity B_ν in potassium vapor increases on passing to shorter wave-lengths somewhat beyond the series limit. The experiments were beset with difficulties and only rather qualitative data were obtained. The results, however, were of considerable significance for they were not predicted theoretically and moreover bore no resemblance to the variation of B_ν in caseium and rubidium.[3, 4] It was suggested[2] that the presence of an abundance of potassium molecules was responsible for the unexpected behavior, a view which was later given support by an investigation by Ditchburn[5] on the continuous optical absorption of potassium vapor. An adaptation of a quite different experimental method has made possible a much more quantitative study leading to results which, though qualitatively in accord with the previous observations, compel a revision of ideas and even suggest that the observed variation of B_ν is an atomic phenomenon after all.

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[1] Williamson, Phys. Rev. **21**, 107 (1923).
[2] Lawrence, Phil. Mag. **50**, 345 (1925).
[3] Mohler, Foote and Chenault, Phys. Rev. **27**, 30 (1927).
[4] Lawrence and Edlefsen, Phys. Rev. **34**, 233 (1929).
[5] Ditchburn, Proc. Roy. Soc. **A117**, 486 (1928).

The experimental apparatus and technique were the same as used in a preceding study of caesium and rubidium.[4] Light from an iron arc source, resolved into wave-length bands by a Bausch and Lomb monochromator (0.2 mm slits) was separated into two portions by reflection and transmission through a quartz plate. The reflected portion passed into the photo-ionization tube and the transmitted portion was focused on a thermopile. The arrangement made possible simultaneous measurement of the photo-ionization produced by and the intensity of the light. The photo-ionization tube was kept at a temperature near 210°C, being a temperature at which the quartz window was not discolored appreciably in a reasonable length of time though high enough to produce the requisite vapor pressure. The same care in distilling and purifying the potassium was used as in the preceding work.

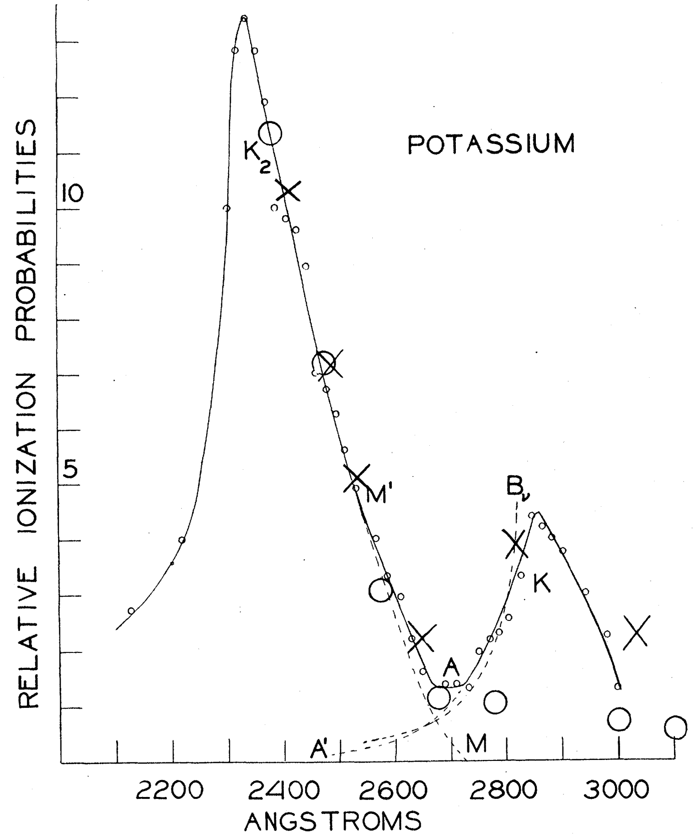

Fig. 1. The ionization per unit light intensity B_ν as a function of the wave-length. The small circles represent the data of the present experiments. The large circles represent earlier observations by Lawrence, and the crosses Williamson's recent data.

The experimental results are embodied in the curve of Fig. 1. The ordinates are the relative values of B_ν for wave-lengths given by the abscissas.

The data were taken at 100A intervals over the whole range of wave-lengths, successive runs having their beginning at wave-lengths 20A apart. This was done to minimize systematic errors introduced by changing conditions in the photo-ionization tube which would have seriously altered the observed variation of B_ν with frequency had the observations been taken at successive intervals of 20A over the whole spectral range. The effects of changing conditions over runs involving 100A intervals were noticeable, though readily corrected for. The various runs were correlated and led to the composite data represented by the small circles of Fig. 1. To compare the results with former work the observations of Lawrence[2] have been plotted as large circles and the observations of Williamson[1] as crosses. Williamson's observations were made with a mercury arc and only his data corresponding to the wave-lengths of the more intense lines are recorded as significant. Lawrence's data represents the average effect of very wide bands of wave-lengths, a circumstance which, coupled with a scantiness of observations (due to the low intensity of the iron arc in the region of 2856A) near 2856A, obscured maximum of B_ν at the series limit. Thus it is seen that both sets of earlier observations are in qualitative agreement with the data represented here. Samuel's[6] observations also are in accord with the present data though his experiments were confined to the region of wave-lengths 2700 to 2900A.

The ionization efficiency B_ν exhibits two maxima, one (K) at the series limit, 2856A, and another (K_2) at 2340A. The variation of B_ν in the region of the series limit is quite similar to the corresponding behavior in caesium and rubidium and it would seem that the ionization by wave-lengths longer than the series limit involves absorption of the principal series lines as in the case of the heavier alkalis. The rate of decrease of B_ν to shorter wave-lengths beyond the limit is also very much the same as in the heavier alkalies down to approximately 2700A. This is illustrated by the dotted curve B_ν, being a plot of

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

which fitted so well the caesium and rubidium observations. Beyond 2700A B_ν rises rapidly to a maximum at 2340A falling off again at 2100A to a magnitude comparable to the 2700A minimum. B_ν at 2340A is about three times its value at 2856A.

Because of the similarity of the maximum $(K)_\nu$ of B_ν at the series limit to the observed variation of B_ν in caesium and rubidium the hypothesis naturally suggests itself that the second maximum (K_2) is due to ionization of potassium molecules. On this view the atomic part of the observed B_ν decreases for shorter wave-lengths to A (see figure) and probably along the extrapolated curve AA'. Thus molecular ionization presumably sets in at about 2700A, and the molecular part of B_ν increasing on passing to shorter wave-lengths to the maximum K_2 at about 2340A, and receding again beyond in the manner shown in the figure. Assuming the atomic extrapolation AA',

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[6] Samuel, Zeits. f. Physik **29**, 209 (1924).

the molecular B_ν curve would follow along the dotted curve $M'M$ yielding a threshold slightly above 2700A. The precision of the data introduces a probable uncertainty in this value of about 20A. The finite bands of wave-lengths also probably introduce a slight systematic error.

This hypothesis of molecules is not new and indeed a considerable amount of evidence has been adduced in its support. Originally, Lawrence[2] interpreted his rather surprising observations of B_ν increasing on passing to shorter wave-lengths as a molecular phenomenon and suggested that an apparent change of slope at 2610A of the B_ν curve marked a molecular photoelectric threshold. Later Ditchburn[5] carried out an experimental study of the continuous absorption of light in potassium vapor. He also concluded that a considerable part of the absorption was due to molecules and by taking observations at different vapor pressures he was able to separate the molecular and atomic contributions to the total absorption coefficient. He was handicapped in the analysis of his data by the unknown, though considerable, effect of the foreign gases necessarily present (pressures 3 cm to 70 cm). However, it appeared that molecular absorption abruptly increased on passing to shorter wave-lengths beyond 2550A. This result was regarded as a confirmation of Lawrence's earlier observations. Ditchburn[7] regarded the molecular absorption to be a process involving dissociation of the molecule plus ionization of one of the atoms. Ditchburn and Arnot[8] have recently shown that photo-ionization produces only atomic ions and therefore if molecules are ionized in appreciable amounts, the process must be just that. He observed, moreover, continuous absorption in the visible region of the spectrum which appeared undoubtedly to be due to molecular dissociation plus excitation of one of the dissociated atoms. On this view the data yielded for the dissociation potential of the potassium molecule the value 0.51 volts.

Thus the more accurate data of the present paper have weakened the strongest argument in favor of the molecular hypothesis. The apparent molecular threshold which was thought to be at 2550A and which was interpreted as measuring a dissociation potential of 0.5 volt comes more nearly at 2700A, corresponding to a dissociation potential of only 0.25 volt. Even with a dissociation potential of 0.5 volt Ditchburn[5] calculated that there were not more than 6 molecules present to every 10,000 atoms (at 550°K) and therefore to account for the results it was necessary to conclude that the absorption per molecule is about 10^4 times the absorption per atom. It is difficult to understand theoretically* such a relatively large molecular absorption coefficient. A lower dissociation potential indicating the presence of many fewer molecules greatly augments this difficulty.

However, there are other rather good reasons for believing that the dissociation potential is greater than 0.25 volt, and perhaps is nearer 0.5 volt. Carelli and Pringsheim[9] deduced a value for the heat of dissociation from observations of the variation of intensity of molecular fluorescence with

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[7] Ditchburn, Cam. Phil. Soc. Proc. **24,** 320 (1928).

[8] Ditchburn and Arnot, Proc. Roy. Soc. **A123,** 516 (1929).

* We are indebted to Professor J. R. Oppenheimer for a discussion of this point.

[9] Carelli and Pringsheim, Zeits. f. Physik **44,** 643 (1927).

temperature when (1) the vapor was saturated and (2) when the pressure was kept constant. Assuming the fluorescence was proportional to the number of molecules present they obtained the values 0.63 volt and 0.53 volt. Ditchburn concluded that the systematic errors in Carelli and Pringsheim's method were such as to yield too high values and that 0.5 volt was a more was a more suitable estimate. Though it appears to the authors (further evidence favoring this view is given below) that the present results are concerned with the variation of the atomic B_ν, it should be emphasized that that the hypothesis of molecules being responsible for the K_2 maximum does not imply that the molecular threshold at 2700A measures with accuracy the dissociation potential. The thermal energies of the molecules are of appreciable magnitudes and could shift the observed threshold considerably. A satisfactory estimate of the transition probabilities corresponding to ionization from various initial vibrational and rotational states to various states of the continuum, involving knowledge of the Franck-Condon potential energy curves, would be necessary to calculate the effect of the thermal energies on the observed threshold.

Williamson's[10] experimental study of the velocity distribution of the photo-electrons ejected from potassium vapor may be cited as excellent evidence favoring the view that the observed variation of B_ν is an atomic phenomenon. He found that the maximum velocity of ejection for the wavelength 2399A to be even somewhat greater than that to be expected from ionization of the atom and there appeared to be no definite low velocity group which would result from molecular dissociation (dissociation potential 0.5 volt) and ionization. Though Williamson's work is very significant, his data are possibly not definite enough to settle the point. An accurate measurement of the energies of the ejected electrons of course would constitute crucial evidence for the correct interpretation of the photo-ionization process and therefore it is hoped that researches in this direction will be continued.

Ditchburn's[5] analysis of his data on the continuous optical absorption by potassium vapor possibly constitutes the best evidence in favor of the here observed B_ν being an atomic phenomenon. By observing the variation of B_ν at several pressures he was able to separate the molecular absorption from the atomic absorption and found that the atomic absorption was a maximum at the series limit, decreased to a minimum near 2700A and rose to a higher maximum again near 2400A. Thus his evaluation of the atomic absorption is quite in agreement with the present observations.

It appears, therefore, that the evidence supports the view that B_ν for atomic potassium vapor does not decrease with wave-length monotonically beyond the series limit as is the case for caesium and rubidium, the continuous absorption beyond the Lyman and Balmer limits and in the x-ray region. One of us (N. E. E.) expects to carry through the quantum mechanical calculation of this effect.*

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[10] Williamson, Proc. Roy. Soc. **A114,** 796 (1928).

* A similar calculation for the photoelectric effect in lithium has been made by Hargreaves, Proc. Camb. Phil. Soc. **25,** 75 (1929).