Lifetimes of Potassium Doublets λ4047–4 and λ3447–6

DAVID SINCLAIR AND HAROLD W. WEBB, *Columbia University*

(Received July 2, 1936)

The lifetimes of the potassium doublets λ4047–4 and λ3447–6 were measured by the a.c. excitation method previously described. A sodium-hydride vacuum photo-cell of special design was used to measure the radiation from a potassium cell containing a hot cathode and two anodes. Measurements were made throughout a range of vapor pressures from 4×10^{-5} mm to 10^{-2} mm. The lifetime of λ4047–4 was found to be 3.79×10^{-7} sec., the lifetime of λ3447–6 to be 8.50×10^{-7} sec., with an estimated precision of one percent. It was shown that the radiation emitted after electron excitation followed a simple exponential law. No change in the measured value of the lifetime was found for either of the doublets throughout the whole pressure range studied. This could be accounted for by the assumption that only 10 percent of the absorbed λ4047–4 is re-emitted at the same wave-length, and similarly for λ3447–6. Measurements made of the variation of the emission with pressure, and of the absorption, were consistent with this assumption.

INTRODUCTION

THE first doublet of the principal series of the alkali metals has been extensively studied and the lifetimes and f values of Li, Na, K and Cs have been measured by absorption and magneto-rotation methods. No direct measurements of the lifetimes of the second or higher doublets have hitherto been made. The ratios of the f values for the first and second doublets have been determined,[1] but since there is more than one transition from the upper level of the second doublet, its lifetime cannot be derived from its f value.

In the present investigation a direct determination was made of the lifetime of the second and third doublets of potassium, each doublet being treated as a single line. The method of measurement was that developed in this laboratory.[2] Potassium vapor at low pressure was excited by electron impact, with a pure sinusoidal exciting voltage applied in such a way that radiation was emitted during the positive half-cycle only. The radiation was measured by a photo-cell to which the same voltage was applied in phase. At low frequency the radiation was all emitted during the positive half-cycle and the photo-current was a maximum. As the frequency was increased, the total excitation being held constant, the photo-current decreased due to the persistence of the radiation, some of which reached the photo-cell during the negative half-cycle. From the relation between the photo-current and the frequency, the lifetime, τ, was calculated as previously described.[3]

APPARATUS

The apparatus is shown schematically in Fig. 1. The potassium excitation cell was a Pyrex tube, containing electrodes C, G, and G'. C was an equipotential hot cathode, consisting of a nickel cylinder 3 cm long and 6.5 mm in diameter, with an internal tungsten heater. The accelerating grid G was a coaxial half cylinder of 9 mm radius. It was made of 1.6 mm mesh nickel gauze and placed in front of the cathode. The electrode G' was a nickel gauze cylinder 2.6 cm in diameter fitted against the wall of the tube, with a curved nickel sheet partition 5 mm in back of C.

The vapor pressure of the potassium in the excitation cell was controlled by the temperature of a small side tube containing the excess potassium. This was immersed in melted Woods metal in a brass cup, the lower end of which was in an oil bath thermostatically controlled to $\frac{1}{4}$°C. The rest of the cell was superheated 50°C above the temperature of the oil bath. The values of the vapor pressure given in this paper are those computed from the temperature of the oil bath, without any correction.

The vacuum photo-cell was a Pyrex tube 4 cm in diameter containing electrodes P, H, and W. The sodium-covered electrode P, a nickel

[1] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, pp. 146–151; S. A. Korff and G. Breit, Rev. Mod. Phys. **3**, 499–501(1932).

[2] H. W. Webb, Phys. Rev. **24**, 113 (1924); F. G. Slack, Phys. Rev. **28**, 1 (1926); H. W. Webb and H. A. Messenger, Phys. Rev. **33**, 319 (1929); R. H. Randall, Phys. Rev. **35**, 1161 (1930); P. H. Garrett, Phys. Rev. **40**, 779 (1932).

[3] Slack, reference 2, p. 2.

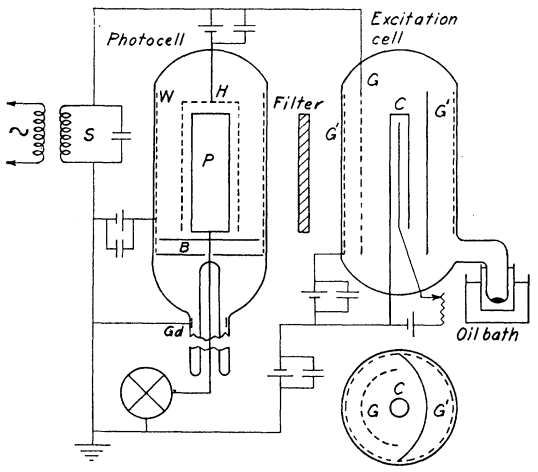

FIG. 1. Schematic diagram of apparatus and electrical circuits.

cylinder 13 mm in diameter and 5 cm long, was supported centrally on a re-entrant glass tube, made 17 cm long to increase the electrical leakage path. As a further precaution, an internal guard ring, *Gd*, which was held at ground potential, was fitted to the walls of the cell. In addition, nickel disk baffles, *B*, prevented evaporation of sodium into the re-entrant tube. With this design, the resistance between *P* and the rest of the tube was about 10^{16} ohms. The sodium-covered electrode H was a coaxial nickel gauze cylinder 19 mm in diameter. Fitted against the wall was a cylindrical electrode *W* of sheet nickel, with a gauze window to allow the passage of radiation. A photo-sensitive sodium-hydride surface was formed on *P* and *H* according to the method given by Nottingham.[4]

In the construction of each cell all metal parts were pre-outgassed and the cells were baked out at 500°C for several hours before distilling in the alkali metals. A liquid-air trap prevented the entrance of mercury into the cells, which were pumped out to a pressure of about 10^{-5} mm and sealed off when cold.

The photo-cell was placed 5 cm from the excitation cell. Between them was a heat insulating partition consisting of alternate layers of wood and metal, except for a window 6 cm long by 3 cm wide. A large part of the heat radiated through this window was absorbed by the filters described below. The temperature of the photo-cell did not exceed 25°C, at which temperature the sodium had little tendency to evaporate and destroy the insulation.

In all observations Corning glass filters were used between the excitation cell and the photo-cell to isolate the doublet under observation; filter No. 511, $1\frac{1}{2}$ mm thick, and No. 428, $3\frac{1}{2}$ mm thick for λ4047–4; and No. 584, 5 mm thick for λ3447–6. Photographs of an iron spark taken through the filters showed that the λ4047–4 filter was opaque to all subordinate series lines and the radiation from the hot cathode, and allowed the passage of one percent of λ3447–4; and that the λ3447–6 filter was opaque to λ4047–4 and allowed the passage of one percent of λ3218–7, the fourth doublet of the principal series. Furthermore, the photo-cell was very insensitive to λ5461 and longer wave-lengths.

D.c. bias voltages were supplied by small dry cells. The a.c. voltage, supplied by vacuum-tube oscillators, was applied to the grids *G* and *H* of the experimental cells by connecting these electrodes to a parallel resonant circuit, *S*, which was loosely coupled to the oscillator. The peak value of this voltage was measured with a vacuum tube voltmeter and could be held constant over the whole range of frequencies used, to within 0.5 percent. For all frequencies the a.c. voltage was shown to be practically free from harmonics by tuning the resonant circuit to the first and second harmonics, for which the voltage was less than 0.5 percent of the voltage when tuned to the fundamental frequency.

The photo-currents were measured with a Compton quadrant electrometer of about 5000 mm per volt sensitivity. The steady leakage current, about 10^{-16} amperes, amounted to 1 to 10 percent of the true photo-current, which was corrected accordingly.

PROCEDURE AND RESULTS

In the calculation of the lifetime, τ, from the measurements made with a.c. voltage applied simultaneously to the excitation cell and photo-cell, the d.c. voltage- or static-characteristics of the two cells should be known. The typical excitation curves, Fig. 2, show the relation between the photo-current and the exciting voltage on *G*, the voltage difference between *H*

[4] W. B. Nottingham, J. Frank. Inst. **205**, 637 (1928).

and P, $H-P$, being held constant. The excitation potential $G-C$, was varied between 0 and 7.5 volts. The wall grid potentials $G'-C$ and $W-P$ were held constant at 1.5 and 6.0 volts, respectively. The photo-currents in the two curves are drawn to different scales.

These curves show that λ4047–4 and λ3447–6 appeared at approximately the theoretical voltages for these radiations, 3.1 and 3.6, respectively. The curve for λ4047–4 is practically linear, whereas that for λ3447–6 departs somewhat from a straight line.

The typical photo-cell curves, Fig. 3, show the relation between the photo-current and the voltage $H-P$, the radiation from the excitation cell being held constant. $H-P$ was varied between -5 and 3. The wall grid voltages were the same as given above. The photo-currents in the two curves are drawn to different scales. It will be observed that for negative voltages on the grid, the current never reaches saturation. The voltage for zero current differs in the two curves by about 0.5 volt, due to the difference in the positive and negative photo-currents and the difference in wave-lengths.

Fig. 4 shows typical curves obtained with a.c. voltage applied simultaneously to the excitation cell and the photo-cell. The vapor pressure and other conditions were the same as for the static characteristic curves. The abscissas are the frequencies. The ordinates are the ratios, R, of the photo-current at high frequency to that at 12,000∼. Such a curve will be referred to below as the $R-f$ curve. The a.c. voltage, which had a peak value of 4.0 volts, was applied in phase to the excitation grid G and the photo-cell grid H. These grids were biased so that the excitation started and the photo-current reversed at the beginning of the positive half-cycle, see Figs. 2 and 3. Since the wall grid G' of the excitation cell was kept 1.5 volts positive with respect to C, all electrons which passed out through G were removed rapidly, thus preventing them from exciting radiation in the negative half-cycle. Similarly the positive potential of 6 volts on the wall grid W of the photo-cell prevented photo-electrons which passed out through H from going back to P in the following half-cycle.

From the experimental observations the life-time, τ, was deduced in a manner similar to that described in the earlier papers[3] on the assumption of a simple exponential decay of the excitation. The excitation, which was confined to the positive half-cycle, was closely given by $A \sin 2\pi ft$ for λ4047–4, and $B \sin 2\pi ft - 0.06C \sin 2\pi 3ft$ for λ3447–6. The radiation emitted as a function of the time was calculated as before. It was conveniently expressed using $t'=t/\tau$ as the time variable and $\psi=2\pi f\tau$ instead of f, giving a curve depending only on the parameter ψ. For different values of ψ the intensity-time curves were constructed. By multiplying each point on these curves by the ordinate of the photo-cell characteristic corresponding to the simultaneous value of the voltage applied to the grid of the photo-cell, new curves were obtained showing the variation of the photo-current with the time, during one complete cycle. By graphical integration, the average photo-currents were then

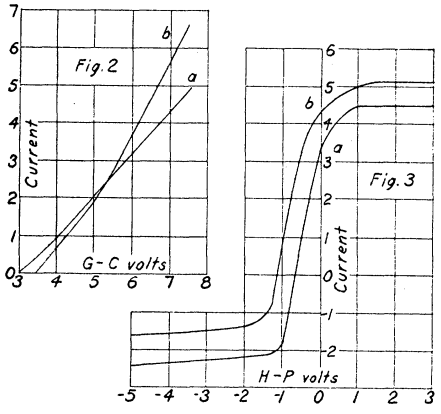

FIG. 2. Typical excitation curves, (a) λ4047–4, $p=2\times10^{-4}$ mm, (b) λ3447–6, $p=10^{-3}$ mm.
FIG. 3. Typical photo-cell curves, (a) λ4047–4, $p=2\times10^{-4}$ mm, (b) λ3447–6, $p=10^{-3}$ mm.

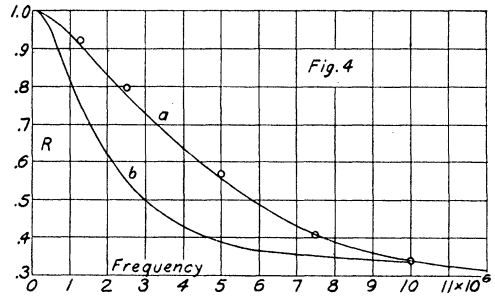

FIG. 4. Typical R–f curves, (a) λ4047–4, $p=2\times10^{-4}$ mm, (b) λ3447–6, $p=10^{-3}$ mm.

found for each value of ψ, and an $R-\psi$ curve was constructed. τ was then obtained from the relation $\psi=2\pi f\tau$ by substituting for any given value of R the corresponding values of ψ and f on the $R-\psi$ and $R-f$ curves, respectively. The most precise results were obtained from the curve in the neighborhood of $\psi=1$, and this part of the experimental curve was determined with very great care by taking a large number of observations.

The mean life of λ4047–4 was found to be 3.79×10^{-7} sec., and the mean life of λ3447–6 to be 8.50×10^{-7} sec. with an estimated precision of one percent.

These values were determined from measurements made at $p=2\times10^{-4}$ mm for λ4047–4 and $p=10^{-3}$ mm for λ3447–6. As the effect of absorption and re-emission within the excitation cell is to decrease the rate of decay of the emitted radiation,[5] τ can be determined only from measurements at such low pressures that the effect of this "imprisonment of radiation" is negligible. Experimentally it is sufficient to decrease the pressure until the observed rate of decay no longer increases, this limiting value determining the correct value of τ. In the present measurements no change in the value of the rate of decay was observed over a range of pressures extending from 4×10^{-5} mm to 10^{-2} mm for λ4047–4, and from 5×10^{-4} mm to 10^{-2} mm for λ3447–6. The pressures at which the precise determinations of τ were made were within these limits and were selected to give the best experimental conditions.

A suspected source of error in these measurements was the effect on the rate of decay of the radiation resulting from the population of the 5^2P levels by transitions from higher levels excited by electron impact. In the case of λ4047–4, the next higher level has an energy difference of 0.3 volt. Since the relative contributions of directly excited radiation and that due to the "cascading" depend on the peak voltage, measurements of the decay rate were also made with three other values of the peak voltage: 2, 1, and 0.5. No difference in the values of decay rate was found, indicating that practically only direct excitation was present. Similar tests with λ3447–6 were made with two other values of the peak voltage 2, and 1.5, with similar results. Additional tests were made with other values of the d.c. bias on G and H. These gave the same value of τ.

To check the behavior of the two cells with high frequency impressed, two tests were made. First, a steady potential was impressed on the photo-cell and the same a.c. and d.c. potentials were applied to the excitation cell as were used for the $R-f$ curves. The photo-current was found to be the same for all frequencies used, 10^3 to 2×10^6 cycles, showing that with constant peak voltage the total energy emitted was independent of the frequency. This served also as a test of variation in wave form. In the second test a constant d.c. potential was applied to the excitation cell while the photo-cell was subject to the same potentials as for the $R-f$ curves, and it was found that the photo-current was the same for all frequencies, showing that the form of the photo-cell characteristic was independent of frequency.

As a further check on the method and especially on the assumption that the radiation excited at any instant falls off exponentially, τ was determined by a second method which did not involve knowledge of the photo-cell characteristics. Using a low frequency for which the effect of the persistence of the excited radiation was negligibly small, the conditions under which the $R-f$ curves were taken were reproduced in the following manner. A half-wave rectified sine voltage of 1000~ was applied across two noninductive resistances, r_1 and r in series; and a variable capacity, C, and the excitation cell were connected in parallel across r. Considering the result for one cycle only, we find that for r_1 large with respect to r, and the current through the excitation cell small with respect to the current through r, the voltage across r at any time is given by:

$$E_r=\text{const. } e^{-t/rC}\int_0^t e^{\beta/rC}\sin 2\pi f\beta d\beta$$

for $0<t<\frac{1}{2}f$. When $t>\frac{1}{2}f$ the voltage, E_r, decreases as $e^{-\beta/rC}$. With a linear excitation characteristic the radiation produced is proportional to E_r, and except for the change in the time scale, the relation between radiation and time at the low frequency is the same as that

[5] Webb and Messenger, reference 2, p. 325.

resulting from the persistence of the radiation at high frequency.[6]

Consequently, if we vary C and plot as ordinates, R, the ratios of the photo-current obtained to that for $C=0$, and as abscissas $rC\omega/2\pi$, we have a curve identical with the $R-f$ curve except that the abscissas are reduced by a factor equal to τ. The points marked by circles in Fig. 4 for λ4047–4 were obtained by this method using the value of τ already found, 3.79×10^{-7} sec. The agreement is satisfactory, affording a valuable check on the method and the assumption that the radiation decays exponentially.

Owing to the fact that the excitation characteristic for λ3447–6 was not a straight line, the above method could not be used to determine τ for this wave-length.

Discussion

As stated above the measured rate of decay of the radiation for each of the wave-lengths studied was found to be the same for pressures at which the absorption was negligible (10^{-4} mm) as for pressures at which the absorption was 90 percent (10^{-2} mm). If at the higher pressures more than a small fraction of the radiation absorbed were re-emitted at the same wave-length, a marked decrease in the rate of decay of the radiation excited in the mass of vapor should have been observed. Webb and Messenger[5] found that because of this "diffusion of radiation" the rate of decay of the λ2537 radiation from a mass of mercury vapor excited by electron impact varied very nearly inversely as the pressure over a 100-fold pressure range. λ2537 when absorbed is practically all re-emitted at the same wave-length. We conclude therefore that in potassium only a small fraction of λ4047–4 when absorbed is re-emitted at the same wave-length, and similarly for λ3447–6.

An atom excited to the 5^2P level can return to the normal state by three processes: first, by radiation of λ4047–4 (4^2S-5^2P); second, by successive radiation of the lines λ27,215–27,066 (5^2S-5^2P), λ12,523–12,434 (4^2P-5^2S), and λ7699–65 (4^2S-4^2P); third, by successive radiation of the lines λ31,597–31,395 (3^2D-5^2P), λ11,772–11,690 (4^2P-3^2D) and λ7699–65 (4^2S-4^2P). Let α be the ratio of the probability of the direct transition to the sum of the probabilities of the two indirect transitions. From the present measurement a maximum value for α of 1/10 is estimated since a measurable change in the rate of decay would have been observed if more than 10 percent of the radiation incident on the photo-cell were re-emitted radiation of the same wave-length.

This estimate is in agreement with that made from a study of the variation in the intensity of the radiation emitted from the excitation cell as a function of the vapor pressure. The cell was placed close to the photo-cell so that the latter received, in addition to the λ4047–4 radiation excited by electron impact, the major part of that which was absorbed and re-emitted at the same wave-length. As the vapor pressure in the excitation cell was increased the radiation increased, first in direct proportion to the vapor pressure, then at a less rapid rate due to the absorption by the outer layers of vapor; and finally the emitted radiation decreased with increase of vapor pressure. This was as expected since the re-emission at other wave-lengths of energy absorbed as λ4047–4 is equivalent to dissipative absorption. From the relation obtained between the emitted radiation and the vapor pressure and from the absorption coefficient previously determined, a value of α was computed equal to $\frac{1}{8}$. However, owing to the difficulty of estimating the effective thickness of vapor layer and other factors, this determination is subject to large error and can be regarded only as roughly confirming the estimate of α made from the lifetime measurements. For λ3447–6 the lifetime measurements also indicate that α does not exceed the above value.

From a study of the anomalous dispersion, Prokofiew and Gamow[7] found for the ratio of the transition probability of the first doublet to that of the second, for the principal series of potassium, a value of 30.3. From magneto-rotation measurements Weiler[8] obtained for the first doublet $\tau_1=2.7\times10^{-8}$ sec. This is equal to the reciprocal of the transition probability, since for this doublet α is equal to unity. The

[6] Slack, reference 2, p. 8.

[7] W. Prokofiew and G. Gamow, Zeits. f. Physik **44**, 887 (1927).

[8] J. Weiler, Ann. d. Physik **1**, 361 (1929).

experimental value of the lifetime of the second doublet λ4047–4 as found above is $\tau_2 = 3.79 \times 10^{-7}$ sec. This is equal to the product of α and the reciprocal of the transition probability for this doublet, since τ equals the reciprocal of the sum of the probabilities of emission from the upper level. This gives $\alpha = \tau_2/30.3\tau_1 = 0.46$, which is considerably larger than our estimate.

It is interesting to compare this with the value $\alpha = \frac{1}{2}$, obtained for the sodium doublet λ3202–3, by Christensen and Rollefson.[9] They illuminated a bulb containing sodium vapor at a pressure of 10^{-4} mm and measured the relative intensities of λ5890–6 and λ3202–3 emitted at right angles to the illumination, from which they computed α. On the other hand Weiss[10] found α to be about 1/25 by comparing the relative intensities of these same doublets emitted by an arc.

The preceding discussion is based on the assumption that all radiation not directly transmitted is absorbed and re-emitted, the mean time for the process being equal to τ. Coherent scattering has been assumed negligible and the pressures were too low for dissipative absorption by collision. The effect of coherent scattering superposed on absorption would be to give too small a value for α as estimated from the lifetime measurements. On the other hand the effect on the results of Christensen's and Rollefson's[9] experiment would be to give too large a value for α.

[9] C. J. Christensen and G. K. Rollefson, Phys. Rev. **34**, 1157 (1929).

[10] C. Weiss, Ann. d. Physik **1**, 565 (1929).

SEPTEMBER 1, 1936 PHYSICAL REVIEW VOLUME 50

The $^1\Sigma^* - {}^1\Sigma$ Band System of Copper Deuteride

MYRON A. JEPPESEN,* *Department of Physics, Pennsylvania State College*

(Received May 8, 1936)

The copper deuteride bands have been photographed with high dispersion and an analysis is given of the $^1\Sigma^* - {}^1\Sigma$ system. The $Cu^{63}D$ and $Cu^{65}D$ isotopic bands are separated and an independent analysis is given for each. From data obtained for the normal $^1\Sigma$ state, ρ for $Cu^{65}D$ to $Cu^{63}D$ is 0.999503 which agrees with the best mass spectrographic data. A comparison with Heimer and Heimer's CuH analysis gives a value of ρ equal to 0.7131 for $Cu^{63}D$ to $Cu^{63}H$. The electronic isotope displacement of CuD relative to CuH is 19 cm^{-1}.

INTRODUCTION

THE spectrum of CuH has been photographed by several investigators.[1–4] None of these has given a complete analysis of the copper isotopic bands. The purpose of the present investigation was to obtain data for a comparison of the hydride and deuteride spectra, and also to make a rigorous copper isotope analysis. After the experimental work and much of the analysis was finished it was learned that the copper deuteride spectrum had been photographed in another laboratory.[5] Since no mention was made of a copper isotope analysis it appeared worth while to complete the present study.

EXPERIMENTAL

The spectrum was excited in a water-cooled metal arc chamber. Deuterium, produced by the vacuum distillation of heavy water onto powdered zinc, was admitted to the chamber and kept at a pressure of 40 cm of mercury. Following the suggestion of Heimer and Heimer[2] we used an anode of bismuth copper alloy and a cathode of pure copper. The arc chamber was evacuated and refilled with deuterium five or six times during a 24-hour exposure. The arc was run from a 220 volt line and carried a current of approximately 3 amperes.

* From a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[1] Jevons, *Band Spectra of Diatomic Molecules* (1932), p. 300.

[2] A. Heimer and T. Heimer, Zeits. f. Physik **84**, 222 (1933).

[3] T. Heimer, Zeits. f. Physik **95**, 321 (1935).

[4] B. Grundstrom, Zeits. f. Physik **98**, 128 (1935).

[5] T. Heimer, Naturwiss. **23**, 372 (1935).